EFFECT OF SEWAGE AND ROCK PHOSPHATE ON THE UPTAKE OF NUTRIENTS

ABSTRACT

A
Thesis
Submitted to
The University of Allahabad
for the Degree of

DOCTOR OF PHILOSOPHY

IN AGRICULTURAL CHEMISTRY AND SOIL SCIENCE

By
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M. Sc. (Ag. Chem.and Soil Science)

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1995

ABSTRACT

Continuous application of sewage to soil has proved beneficial due to its high nutritive value resulting in improved soil fertility. Besides N, P and K, the sewage contains toxic metals as well viz. Cr, Cu, Pb, Cd, Fe, Zn, etc. A continuous use of sewage for irrigating crops may thus cause heavy metal accumulation in soil to an extent that may prove toxic to crops grown in contaminated soils. Excessive amounts of such heavy metals in turn may cause clinical problems in animals and human beings.

Hence there is a need to findout means by which the toxic amounts of heavy metals in crops could be reduced. The present study was therefore, undertaken with a view to reduce the availability of heavy metals, if possible, by means of adding rock phosphate to the soil receiving sewage irrigation.

The rock phosphate generally contains phosphate which is slowly made available in the soil.

EXPERIMENTAL :

The experimental work has been divided into two parts. In the first part the response of Mussoorie

Rock Phosphate (MRP) on the growth and biomass of vegetable crops viz,. fenugreek, spinach, fenugreek and radish was studied in sequence under field conditions, using sewage for irrigating the soil. In the second part the changes in pH, EC, CEC, organic carbon, macro, micro nutrients and heavy metals of treated soil were determined.

EXPERIMENTAL LAYOUT:

The experiments were conducted at Sheila Dhar Institute research farm, selecting an area of $18m^2$ which was divided into microplots of $1m^2$ area.

The number of treatments were six with three replications. Experimental plots were treated with increasing doses of MRP viz, 100, 200, 300, 500 and 700 kg/ha.

MRP was added before sowing each crop, except in experiemnt II, in which residual effect of MRP was studied with spinach. All the plots were irrigated with sewage water, which is readily available in the farm and is obtained from the nala flowing nearby.

1. **BIOMETRIC STUDIES :**

Fenugreek, spinach, fenugreek and radish were

grown in succession in MRP treated and sewage irrigated plots. The height was recorded after 15 days interval.

The crops were uprooted after 60 days of germination and fresh weight of biomass was found out.

2. CHEMICAL ANALYSIS OF PLANTS AND SOILS:

(i) Plant analysis:

Plant samples were digested with triacid mixture and analysed for heavy metals viz, Zn, Cu, Cr, Pb and Fe with the help of Atomic Absorption spectrophotometer (AAS). Valuable help from IFFCO is gratefully acknowledged.

(ii) Soil analysis:

Soil samples were collected before the experiment, and after the termination of experiment. N, K, CEC, EC were determined by methods, given by Jackson (1973). Organic carbon was estimated by modified Walkely-Black's method, available P was determined by Olsen's method (1954) and pH was measured by Elico Model L-110 pH-meter. Analysis of heavy metals was done by AAS, using Lindsay and Norvell method (1978), using DTPA for extracting the soil.

RESULTS AND DISCUSSION:

Response of Sewage and MRP:

(i) Height, biomass/yield of crops:

A distinct effect of sewage and sewage alongwith MRP on height and biomass of various vegetable crops was observed. Increasing doses of MRP gave better response on the height and biomass of crops in comparison to sewage application alone. The residual effect of MRP was also observed.

(ii) Uptake of heavy metals:

The uptake of heavy metals by plants in sewage irrigated plot was greater than combined treatment of sewage and MRP. With increasing doses of MRP the uptake of heavy metals reduced and the available amounts in soil also decreased.

The uptake of heavy metals by different crops varied. The order was:

Fe> Zn> Cu> Pb> Cr

3. CHANGES IN SOIL :

Organic carbon, EC, CEC, N, P and K were found to have increased insoil after growing four crops. The available P was higher due to additions of MRP. Organic carbon also increased due to cropping and

sewage irrigation.

Conclusions:

The results show that repeated application of sewage leads to accumulation of heavy metals in soil and these metals are taken up by vegetable crops.

MRP addition helps in reducing the availability of heavy metals in soils as well in their uptake by crops.

It is thus beneficial to fortify sewage irrigation by adding a cheap source of P such as MRP to the soil in order to reduce uptake of heavy metals by vegetable crops.

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DEDICATED TO MY

REVEREND PARENTS

SHEILA DHAR INSTITUTE OF SOIL SCIENCE
UNIVERSITY OF ALLAHABAD
(Established in 1935)

Lajpat Rai Road
Allahabad - 211002
U. P.
INDIA

Dated..............19

Prof. S.G. Misra
Ex- Director,

CERTIFICATE

This is to certify that Mr. Devi Dayal Pandey, M.Sc. (Ag. Chemistry and Soil Science) conducted his research work under my supervision on the topic, "Effect of Sewage and Rock-Phosphate on the uptake of Nutrients" for the award of degree of Doctor of Philosophy in Agricultural Chemistry and Soil Science, University of Allahabad. To the best of my knowledge the experimental observations and data presented in the thesis are genuine and original.

S.G. Misra
(S.G. Misra)

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I wish to express my deep sense of gratitude and indebtedness to my revered "Guru ji" Prof. S.G. Misra, Ex-Director, Sheila Dhar Institute of Soil Science, University of Allahabad, for his continued interest, valuable suggestions and encouragement during the course of this work.

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Dayal

ALLAHABAD **DEVI DAYAL PANDEY**

October - 1995

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LIST OF ABBREVEATIONS

AAS	:	Atomic Absorption Spectrophotometer
CEC	:	Cation Exchange Capacity
Concen	:	Concentration
cm.	:	Centimeter
C mol.(p+) kg-1	:	Centi Mole Per Kilogram
FYM	:	Farm Yard Manure
g	:	Gram
ha	:	Hactare
kg	:	Kilogram
lb/A	:	Pound Per Acre
m.e./100gm	:	Milli Equivalent Per 100 Grams
MRP	:	Mussoorie Rock Phosphate
NPK	:	Nitrogen, Phosphorus, Potash
pH	:	Antilogorthim of H^+ ion Concentration in soil.
ppm	:	Parts Per Million (Concentration)
r	:	Correlation Value

CHAPTER I

CHAPTER - I

INTRODUCTION

It has been estimated that the water requirement of one lakh urban population at the rate of 100 liters per day per person will be around 10^7 million liters per year. This quantity will be sufficient to irrigate more than 10^5 hectares of rice per year at 100 cm of water per crop or 3×10^5 hectares of other cereals or 50,000 hectares of sugarcane even at 10 per cent collection efficiency level. Assuming three tones to be the average yield of irrigated food crops, this amount of water would give at least three lakh tones of rice or nine lakh tones of other cereals or 50 lakh tones of sugarcane (5 lakh tones of sugar).

The domestic and industrial waste waters amenable for crop production can help to increase the irrigated area by 170.4×10^3 hectares in the country. The prevention of environmental pollution through recycling of waste is difficult to quantify but it will be very much valuable in view of the clean environment which is a burning need.

In addition to the above, the demands on the

limited available water resources from industries is also on the increase. Because of this, the quantum of water available for agriculture is dwindling day by day.Added to this, the present trend to adopt commercial agriculture growing of high value high return crops in place of food crops, has further aggravated the water availability for food crops.

Another dimension to this problem is the fact that above sectors not only utilise the available water but also discharge considerable amount of waste water (effluent into the nearby lakes, tanks, rivers, seas, land mass etc.) thus polluting the same. Economic disposal of sewage in the urban areas has been a problem since very few of them have good underground/open drain system. Even in cities which are partially covered with such system, they were planned to meet the needs of the population at that time. The same system is unable to meet the expanding demands subsequently.

In view of this, reuse of waste waters in agriculture has become a necessity. In many arid and semi-arid countries around the world which are faced with acute shortage of water, the reuse of sewage water in agriculture is considered as an important strategy

for conserving the water reserves. In humid and temperate countries on the other hand, agricultural use of sewage offers a safe method of disposal of sewage, there by reducing water pollution problems associated with other disposal techniques. In addition to this, use of sewage waters in agriculture would be beneficial due to the high nutritive value of the sewage and its ability to improve the soil fertility.

NATURE OF SEWAGE:

Sewage is the waste water of a community. It may be purely domestic in origin or it may contain some industrial or waste water as well. Sewage is a grey turbid liquid which has an earthy but inoffensive odour. It contains large floating or suspended solids (such as faeces, rags, plastic containers, maize cobs), smaller suspended solids (such as partially disintegrated faeces, paper, vegetable peel) and very small solids in colloidal suspension as well as pollutants in true solution. In hot climates, sewage can soon lose its content of dissolved oxygen and so becomes septic. Septic sewage has a most offensive odour, usually of hydrogen sulphide.

Municipal sewage is defined by World Health Organisation (WHO 1973) as the spent water of the

community, consists of water carried waste from the residents of commercial buildlings and industrial plants and surface and ground waters that enter the sewage system.

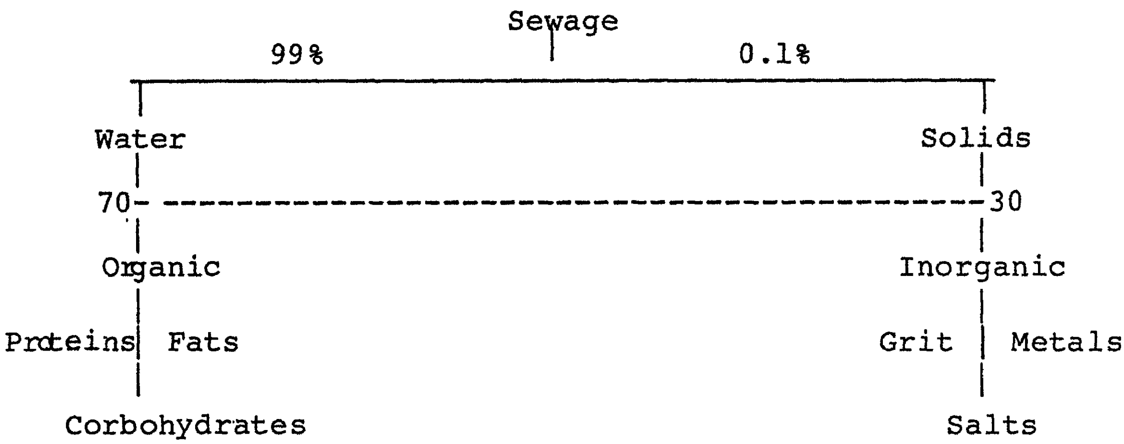

Figure : Composition of sewage : From T.H.Y. Tebbutt. Principle of water Quality Control. Pergamon Oxford (1970).

Sewage is a community liquid waste and primarly consists of used water with hardly 0.1% of solids made up of inorganic and organic matter. When fresh, it consists of faeces, urine, soapy wastes, garbage, rags and grit. Sewage varies considerably in strength and composition from town to town due to the communities, the nature of their diets and per capita water consumption.

Untreated domestic sewage contains 50-150 mg/l grease and oils, and the inclusion of industrial waste water, especially from the food industry, may considerably increase the oil and fat levels. However, more than 65% of the grease and oils are removed by the flotation method used in primary treatment. Typical contents of organic and inorganic suspended solids range from 100-350 mg/l in raw municipal waste water, and the average pickup is estimated at 105 g capita^{-1} day^{-1}. The suspended solids content is an important parameter in evaluating the suitability of sewage effluent for irrigation, since these solids may clog both the soil pores and components of the water distribution system, specially small orifices.

In areas where industrial effluents are discharged to sewage treatment works, many synthetic organic compounds may be present in the raw sewage. Pollutants commonly occuring under such circumstances include aliphatic and aromatic hydrocarbons, petroleum hydrocarbons, benzenes, phenols, PAH (Polynuclear aromatic hydrocarbons), halogenated (particularly chlorinated) aliphatic,alycyclic and aromatic compounds organochlorine pesticides, PCB (Polychlorinated biphenyls) and phthalate esters. In addition to

industrial effluents as sources of organic micropollutants in waste water it is evident that domestic sewage contributes a low level background concentration of trace organic contaminants to raw sewages either through usage or as the result of the contamination of products during manufacture.

Table 1.1: Organic micropollutants in sewage sludge

Compounds	Sample type	Concentration
Polynuclear aromatic hydrocarbons (PAH)	Primary and digested (Germany)	1.6-6.0 mg/kg
	Primary sludges activated sludges (UK)	2.6-10.0 μ/g 0.09-16.0mg/kg
Polychlorinated biphenyls (PCB)	Disgested sludge (USA)	765.0 mg/kg
Lindane	Primary sludge and digested sludges	0.01-0.93 mg/kg
DDE	Primary and digested (UK)	0.01-0.49 mg/kg
Organophosphorus	Primary sludge	500-600 μ/g

Sewage effluent varies widely in its composition, organic materials, nitrogen, phosphorus, oils, phenols, trace elements of dissolved salts and microorganisms.

Raw sewage water contains many microorganisms (bacteria, viruses and parasitic protozoa) which may be pathogenic and parasitic worms. Coliform or fecal coliform counts serve as standard indicators of microorganism contamination of sewage water. Typical raw domestic sewage contains 10^7-10^9 coliform per 100 ml. Biological treatment and disinfection drastically reduce the number of fecal coli to the acceptable level for irrigation water.

Researches on other micro organisms in sewage or sewage irrigated soils are actually very few. Effluents receive large number of fungal species in the treatment plants and also discharged into the crop fields. Soil micro organisms play a very important role in soil fertility. The sewage of domestic origin, metabolic wastes, animals, household pesticides, vegetables and other food materials of kitchen disposal units have certainly some influence on the beneficial pathogenic micro organisms in soil. Soil microbiology and Pesticides Laboratory of Botany Department, Marathwada, University, Aurangabad (India) identified these problems arising from sewage irrigation and has carried out researches on the influence of sewage on soil micro organisms since 1979. Experiments were conducted

on the farms irrigated with untreated sewage at Aurangabad. Sewage irrigation supported the population of N-fixers such as Azotobacter, Rhizobium and also fungal organisms supporting organic matter decomposition. As many as 51 fungal species were identified from the fields growing tomato, cabbage, pumpkin, banana, brinjal, lucerne, maize and sugarcane. Potential pathogens like Aspergillus niger, A. flavus, Alternaria sp., Colletotrichum sp., Helminthosporium sp., Phytopthora sp., Rhizoctonia bataticola, Fusarium oxysporum etc. were noteworthy on record.

NUTRIENT VALUE OF SEWAGE:

Analysis of samples of sewage from different cities of Punjab showed their C/N ratio varied from 2 to 24, total N from 0.26 to 2.99 percent, phosphorus from 0.02 to 0.29 percent, potassium from 0.30 to 1.26 percent, calcium and magnesium from 2.24 to 24.32 percent and organic matter from 3.11 to 28.90 percent.

The average composition of typical raw and treated sewages is given in Table 1.2.

Table 1.2 : Mean values of nutrients in raw and treated sewages (mg/l).

Nutrient	Raw Sewage	Treated Sewage
Total N	66.2	57.2
Total P_2O_5	22.6	37.0
K_2O	42.1	17.6
Ca	182.0	-
Mg	568.0	-
Na	132.0	-
Fe	1273.0	856.0
Mn	344.0	205.0
Zn	685.0	87.0
Ni	87.0	50.0
Cu	112.0	68.0
Pb	109.0	942.0
Cr	87.0	25.0
Co	87.0	50.0
Cd	12.0	10.0
B	295.0	135.0

Source : Sarkar, 1982

The ideal management practices on sewage farms call for application of waste water only in such volumes as suit the need of the crops being raised.

Ignorance about the nutrient composition of waste water further aggravates the imbalance in the contents of various plant nutrients. Sewage farming can be effectively followed for soil affected by drought and the consequential moisture stress conditions. There are reports of high fodder producing crops like berseem, lucerne and oats have been grown in sewage farms in North India and hybrid nappier, high yielding fodder sorghum, fodder cowpeas, sesbania, rhodes guinea, setaria and paragrass in South India.

The sewage is useful source of nitrogen, phosphorus, potash and other micronutrients for crop plants. Its application to land should be timed to gain the maximum benefit from the nitrogen which it contains and according to the requirement of the crop.

The manurial value of sewage in this country has been estimated to be about 45000 tones of Nitrogen, 30,000 tones of Phosphorus and 23000 tones of Potash. Thus sewage irrigation has its prospects in future. However, the present utilization of waste water is only about 0.31% of the total potential. The average NPK content in Indian city sewage is 50 ppm N, 15 ppm P_2O_5 and 30 ppm K_2O. Untreated sewage from Haryana shows much less P_2O_5 and higher K_2O and lesser micronutrients.

Table 1.3 : Characteristics of untreated sewage of Haryana (mg/l).

Characteristics	Range	Mean
Nitrogen	25.38-97.58	48.26
Phosphorus	4-12.0	7.0
Potash	27-152.0	72.0
Sulphur	19-60.0	34.0
Zinc	0.13-.90	0.34
Iron	0.59-21.0	10.84
Copper	0.06-0.61	0.20
Manganese	0.25-0.60	0.30

By : C.S.S.R.I. (Karnal)

Chemical characteristics of sewage water vary with the source of the potable water supply, the sewage system, the season and the nature of industrial discharge into the system. A major concern in using sewage effluents for irrigation is the presence of high concentration of hazardous constituents, such as trace elements (heavy metals), stable organics and complex synthetic micropollutants. Some of these e.g. Zn, Cd, Cr, Cu, and Ni can be harmful to plants (Phytotoxic) at excessive levels. However, the concentration in most waste water are well below the toxicity level for all crops, and phytotoxicity may occur only as a result of long term accumulation in the soil. Heavy metals such

as cadmium, chromium and lead can be taken up by plants resulting in toxic concentration in the food chain or pollute ground water and surface water by deep percolation or runoff.

Table 1.4: Concentrationof trace elements in raw and the treated municipal effluents and the permissible level in irrigation water[a] and uper limit for drinking water for livestock[b].

(mg/l)

Elements	Raw Wastewater Range	Median	Water Quality Criteria for Irrigation[c] Long Term	Short Term[d]	Upper Limit for drinking water (livestock)
Arsenic (As)	<0.0003-1.9	0.085	0.1	10.0	
Cadmium(Cd)	<0.0012-2.1	0.024	0.01	0.05	
Chromium(Cr)	0.0008-83.3	0.400	0.1	20.0	
Copper(Cu)	0.0001-36.5	0.420	0.20	5.0	
Iron(Fe)	-	-	5.0	-	Not needed
Lead(Pb)	0.001-11.6	0.120	5.0	20.0	0.1
Mercury(Hg)	0.0001-3.0	0.110	-	-	0.01
Zinc(Zn)	0.001-28.7	0.52	2.0	10.0	24.0

a Chang & Page (1983), Page & Chang (1985).

b Ayers & Westcol (1985)

c The maximum concentration is based on a water application rate of 1200 mm/yr. In case of high rates, the maximum concentration should be adjusted accordingly.

d For use of fine-textured soils.

HEAVY METALS LOADING IN SEWAGE:

The term heavy metal indicates a metal with relatively high density (Anderson 1976).

From an environmental standpoint, the heavy metals can be categorized as:

(I) Those derived from the soil parent material but that exist in such abnormally high amounts or are so readily available that they contribute a threat to the health of plants and animals.

(II) Those that are introduced into the soils as toxic pollutants through industrial effluent , sewage sludge, contaminated ground water and through atmospheric transport. These heavy metals although not essential for plants and animals, may accumulate in plants and cause serious toxicities in animals that feed on them. Sludge retains between 50 to 90% of the heavy metals.

Table 1.5 : Maximum amount of metal suggested for agriculture soils treated with sewage-sludge.

Metal	Maximum amount of heavy metals (lb/A) when soil Cation exchange (m.eq./100 g) is		
	<5	5-15	>15
Lead	440	880	1760
Zinc	220	440	880
Copper	110	220	440
Nickel	110	220	440
Cadmium	4.4	8.8	17.6

Source : Sommers et al. Purdue Uni. A.Y. 240 (1980).

Table 1.6 : Concentration of selected elements in sewage-sludge (mg/l)

Elements	Sommers		furr et al.	Chaney et al.	
	Range	Median		Range	Median
As	6-230	10	3-30	-	-
B	4-760	33	16-90	-	-
Cd	3-3410	16	7-444	1-970	13
Co	1-18	4	4-18	-	-
Cr	10-9900	890	169-14000	-	-
Cu	84-10400	850	458-2890	240-3490	790
Mn	18-7100	260	32-527	-	-
Ni	2-3520	82	36-562	10-1062	42
Pb	13-19700	500	136-7627	52-4900	500
Zn	101-27800	1740	560-6390	-	-

: Sommers (1977), Furr. et al.(1976) and Chaney et al. (1977) have reported metal concentrations of sewage sludges covering a wide range in this table.

Application of sewage sludge to agricultural land is being viewed with concern and it has become a challenge to dispose it in a way that is environmentally acceptable, economically feasible and is least hazardous to human health. The raw sewer water (sewage) and sludges contain beneficial nutrients (such as NPK) as well as to toxic metals (such as Cu, Cr, Fe, Zn, Pb, Cd, Ni, etc.). These waters are used for irrigating forage and vegetable crops in the immediate surroundings of their disposal sites. A long term use of raw sewer waters for irrigating crops may cause metal accumulation in soils to such an extent that they may become toxic to plants (Kirkham, 1983). The uptake of heavy metals by plants is governed by their concentration in the soil solution. Thus, the crops grown in contaminated soils may accumulate heavy metals in excessive quantities which, in turn, may cause clinical problems in animals and human beings.

POLLUTING STRENGTH OF SEWAGE:

The waste from the manufacture of organic chemicals impart to the receiving wastes odours and tastes that are almost impossible to eradicate by water treatment plants. Chemicals and toxic metals like chromium and copper inhibit biological activity in the receiving waters and sewage treatment plants and may render the stream waters unfit for further use.

Excessive concentration of suspended solids settling in receiving waters smother aquatic life. These considerations emphasize the need for satisfactorily treating industrial waste before they are discharged into the receiving streams in order to alleviate or prevent water pollution. The persistence of chemicals in soil is much longer than in other components of the biosphere and contamination of soil, especially by heavy metals, appears to be virtually permanent. Metals thus accumulated in. soils are depleted only slowly by leaching, plant uptake and erosion.

Heavy metals enter soil through different routes and slowly accumulate there. Routes by which soil can be contaminated with heavy metals are dust and rainfall.

Heavy metals, usually added to the soil relatively in small amounts mostly find specific adsorption sites in the soil where they get retained very strongly, either on the inorganic or organic colloids. There are, however, certain less strongly adsorbed metals such as cadmium.

HEAVY METALS AND ASSOCIATED PROBLEM:

Some heavy metals are essential plant nutrients. However, sewage sludge, particularly from highly industrialised areas or other sources, contains heavy metals in amount that may pose toxicity problems.

The relationship between trace element and environmental quality is based upon the need to safeguard man's health. Trace elements are linked to health because of the functions they fulfill in physiological process. Where these functions are of a catalytic nature, the trace element involved nearly always will be a heavy metal.

Heavy metals accumulate in biological system even at the lowest-level of development. The order of affinity of heavy metals for plankton was given as Zn> Pb> Cu> Mn> Co> Ni> Cd and for brown algae as Pb> Mn> Zn> Cu> Cd> Co> Ni (Fed. Water-Poll. contrast Adw

1968).

Contaminant Pb in soil is naturally produced by weathering of native Pb-bearing soil minerals. Contaminated Pb reaching the soil from various sources enters a new cycle of processes following incorporation into the surface layer. This may alter its availability to plants.

When heavy metal enriched wastes are applied to land they are subjected to various interactions with soil and get distributed among different fractions.

The bio-availability, mobility and chemical activity of heavy metals in soil depend on nature of soil and types of heavy metals. Highly acidic condition (pH<5.0), low CEC, and organic matter favour greater availability of heavy metals to plants whereas, in calcareous soils and those with high CEC and organic matter the bio-availability of heavy. metal is appreciably low. The potential uptake of heavy matals by plants depends on types of heavy metals which plants can assimilate. Thus available metal status of soil is more important than its total content.

In general, the plants are excellent barrier to check the translocation of heavy metals from the soils

to consumable plant parts via root absorption except for certain accumulator species. This is specially true for Ni, Cu and Pb. Further Ni and Cu have added protective mechanisms of preeminence of phytotoxicity. Threshold phytotoxicity values for Cu and Ni are 30 and 25 mg/Kg respectively, thus the plants die or fail to grow much before they accumulate a metal toxic to human beings. Lead is physiologically non-essential and potentially harmful metal which may cause unsusceptible adverse effects on plants and animals. A large number of food, forage and ornamental crops have been shown to be damaged by Pb pollution.

If excessive concentration of Pb are reached in the environment there could be a quick and dramatic reduction in plant growth under conditions of phosphate deficiency (Koeppe and Miller 1970). The curtail values results from various type, of leaf damage, of growth, decreased size and yield of fruits and destruction of flowers.

Lead is nearly always present in soils although in small amounts. The solubility of lead in soil increases with acidity and in acid soils, it is accumulated by plants which may contain even toxic amounts of Pb. Lead reaches soil and plant cover as an

aerial deposit and also through precipitation, irrigation water, mine drainage, leaf litter, pesticides, weedicides, petrol and fertilizers. The concentration of Pb in soils decreases with distance from the source. Pb deposition is more common in road sides and lead mine and industrial areas.

Cr in soils can be found only in very small amounts and yet it is this source which has been reported to modify the plants behaviour to a greater extent due to its direct and indirect effects. Thus there is a need to evaluate the Cr status of soil so as to predict plant uptake as well as plant behaviour. Cr compounds that were slightly available exerted a stimulatory effect on plants, as compared to a toxic action exerted by those compounds of Cr that were readily soluble and readily taken up by the plants for which no essential function for Cr has been shown in plants or in animals.

Cr is carcinogenic and a toxic metal and was found to cause skin, respiratory and gastric diseases among the workers employed in chromatic industries.

The soil iron available to plant is affected by various soil reactions. Organic matter in acid soil

normally increases the content of available iron. Usually a deficiency of iron causes chlorosis in plants but an unbalanced ratio of iron and mangnese in soil may also cause iron deficiency. Most factors which have an effect on the uptake of iron regulate its degree of oxidation Both ferric (fe+++) and ferrous (fe++) ions are present in soil as well as in plant. Fe content in different sewage samples vary from 6.7 to 7.2 mg/l. FAO (1985) reported 5 mg/l as maximum concentration of iron.

Copper in large amounts is toxic to plants. Toxicity symptoms commonly include reduced shoot vigour, poorly developed and discolored root system, and leaf chlorosis. Toxicities are uncommon, occuring in limited areas of high natural availability of copper, after additions to soil of materials containing considerable concentration of copper, such a sewage-sludge, municipal composts, pig and poultry manures, and mine wastes, and from repeated use of copper-containing pesticides such as bordeaux mixture, $CuSO_4$ alone, and copper oxychloride.

Table 1.7 : Range of concentration in soils and plants of inorganic elements that sometimes occur as environmental contaminants.

(in ppm)

Elements	Common range	
	Soils	Plants
Arsenic	0.1-40	0.1-5.0
Boron	2.0-100	30-75
Cadmium	0.1-7.0	0.2-0.8
Copper	2.0-100	4.0-15.0
Fluorine	30-300	2.0-20.0
Lead	2.0-200	0.1-10
Manganese	100-4000	15-100
Nickel	10-1000	1.0
Zinc	10-300	15-200

Source : From Allaway (1970).

SEWAGE DISPOSAL AND ASSOCIATED PROBLEMS :

The right way to dispose off town sewage is to apply if continuously to land, and it is only by such application that the pollution of rivers can be avoided (First commission on sewage disposal, England). But continuous application will lead to accumulation of heavy metals (Johnson, Hinsley, Joiner

David, 1974). The disposal of sewage, sewage effluent: and industrial waste water are utilized where inlan cities are located. Raw sewage when discharged int water for disposal by dilution should be as fresh a possible and preferably free from floating matters an solids capable of early sedimentation. The genera standards for sewage effluents discharged into strea for final disposal by dilution are:

(a) The five-day 20°C BOD should not exceed 20 mg/l

(b) The suspended solid content should not excee 30 mg/l (Mahida 1981).

Table 1.8 : Standard for the effluents to be discharge on land.

Characteristics	Tolerance limi
pH	5.5-9.0
Total dissolved solids mg/l (max.)	2100
Sulphates (as SO_4) mg/l (max.)	1000
Chlorides (as Cl) mg/l (max.)	600
Present Sodium (max.)	60
Biochemical Oxygen Demand for 5 days at 20°C mg/l (max.)	200
Oil and grease (max.) mg/l	20
Boron (as B) mg/l (max.)	2
Cyanides (as Cn) mg/l (max.)	0.5

Hexavalent Chromium (as Cr) mg/l (max.)	1.0
Zinc (as Zn) mg/l (max.)	10
Ammonical Nitrogen (as N) mg/l (max.)	100
Copper (as Cu) mg/l (max.)	3.0
Nickel (as Ni) mg/l (max.)	3.0
Total Mercury (as Hg) mg/l (max.)	0.01
Selenium (as Se) mg/l (max.)	0.1
Lead (as Pb) mg/l (max.)	0.5
Arsenic (as As) mg/l (max.)	0.5
Cadmium (as Cd) mg/l (max.)	5.0
Radioactive materials Alpha emitters UC/mg/l (max.)	-9
Beta emitters UC/mg/l (max.)	-8

Courtesy : U.P. Pollution control Board, Pragat: Kendra, IInd Floor-Capoorthala Complex Aliganj, Lucknow, Dated 19.9.92. By orde: Smt. Reeta Sinha, Chairman, U.P. Pollutio: Control Board.

At present a number of agencies have been set up in each country to monitor the use of waste waters and also to see that pollution hazards are eliminated or at least minimised. These agencies have set up their own standards, many a time based on those in force in othe: countries and also based on their own background. Fo:

example, standards have been fixed for the use of sewage/effluents by the Pollution Control Board and they insist that the effluents should be treated to that extent and then only used for irrigation. In this one factor that is ignored is the quality of water needed for irrigation which is not the same as that for drinking water. Another fact that has been completely ignored is that even if the soil is loaded with high quantities of heavy metals, still the toxic effect on plants depends upon the available quantities of those and not on the total quantity present in the soil. Even the estimation of the available nutrients is not a definite one. Different workers have used different extractants and have come to certain conclusion based on the behaviour of a particular crop or variety. As there is considerable amount of these elements the generalisation made by many are erroneous in several respects.

Added to this, there is considerable amount of differences in the rate of mineralisation, volatilisation, movement etc. of these metals when these studies are conducted under tropical conditions in contrast to the temperate/humid climates. This has also not been taken into account while considering the

applicability to data collected in other countries.

Another factor that has to be considered is the technologies adopted in fixing the toxic limits. In many cases, different levels of these elements in inorganic form have been used in the experiments and toxic levels reported. But in sewage/sludge/effluents, most of the elements are in organic combinations and their solubility and release pattern is entirely different from that of inorganic forms. These methodologies have led to fixing up very low values for toxic limits.

Still another factor that has been totally ignored by those who raise the myth of biomagnification of toxic elements in the food chain in the economic conditions as well as cooking and eating habits of a normal citizen in many countries. When one considers the amount of any vegetable, foodstuff etc, that is consumed every day by an individual and its heavy metal/toxic element content, then the intake is very small and is not likely to cause any serious damage. Added to this, no house cooks the same vegetable every day even throughout the weeks, not to talk of month or year. In that case it is likely to be taken by an individual over a span of time to be very low. Added

to this is the processing that the food stuffs underg before being cooked. As has been shown by th autoradiograph studies, in many cases the toxi elements accumulate in edible parts of plant which i normally discarded in processing. Further, the washing peeling, treating with water like tamarind water whic contains organic acids etc. reduce the contents o heavy metals considerably due to their solubility Hence, the question of toxicity to human being does no arise. Added to this further is the various dietr habits developed in each region over years which take care of the problem of accumulation of toxic element in the body of human being. One of the examples is th practice of taking at least a part of "Monthan" banan by people of Kerala State practically every day.

Sewage along with phosphatic material offers very attractive source for irrigating agricultural lan round the cities in order to grow vegetable crops.

The present study was carried out with th following objectives in view.

1. To study the quality of sewage for irrigation.
2. To study the effect of sewage irrigation on th growth and yield of vegetable crops.

3. To study the effect of Mussoorie rock phosphate (MRP) alongwith sewage on the growth and yield of vegetable crops.
4. To find out the pattern of uptake of heavy metals by vegetable crops.
5. To study the changes in soil as a result of various treatments.

* * * * *

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CHEPTER II

CHAPTER-II

ROCK-PHOSPHATE AS AN AMENDMENT: GENERAL REVIEW:

About 30% of the cultivated land in India (i.e. about 49 m ha.) is believed to be acidic in nature, of which almost 40% are medium to strongly acidic. These are indeed the soils which offer maximum possible scope for the utilisation of rock phosphate as a fertiliser.

The rock phosphate being a natural mineral apatite is itself water insoluble. There has been considerable interest in studying the efficiency of rock phosphate for direct application to soil. This is because about 60% of the 122-136 million tones of rock phosphate in India are considered to be unsuitable for use as raw material for manufacturing fertilizer. Indian phosphate rocks, in general, have low reactivity. Mussoorie rock phosphate, the most reactive among them, is about 25% as reactive as the Carolina rock phosphate. Although directly applied, rock phosphate accounts for 1% of the fertilizer P in India, Considering its future potential and interesting research work, the subject merits an 'indepth discussion.

Its composition varies widely not only from source to source but within the same deposit as well. The composition may vary depending upon the depth and location of the deposit and its origin. This variability is probably responsible for the known inconsistency in results with the use of rock phosphate, under similar agro-climatic conditions.

Almost all phosphorus in rock phosphate exists as water insoluble tri-calcium phosphate in the apatite constituent of the rock. Therefore, the initial crop growth and development often suffer when rock phosphate especially with low reactivity is used alone in a non-responsive soil such as those having pH. 6.0 and above and low P fixing capacity and low degree of aluminium saturation.

Use of rock phosphate is often confined to acid soils, plantation and long duration field crops, crops having finer root system, etc. The apathy is that neither the role of soil properties not that of root configuration and nature of plant species have received due attention with respect to the efficient utilisation of rock phosphate.

Despite the fact that there are huge and

widespread reserves of material which could be used as a direct fertilizer without any benefication etc., only two types of rockphosphates viz. Mussoorie and Purulia Rock Phosphate are commercially available on a limited scale.

EFFICIENCY OF ROCK PHOSPHATE:

In many case, first residual effects are longer than direct response so that terminating experiments after one or even two crop can not show the full potential of rock phosphate as fertilizer. A number of factor, control the efficiency of rock phosphate.

(a) SOIL:

Generally the efficiency of rock phosphate increases with falling soil pH. It is debatable whether rock phosphate is more efficient in highly P-deficient acid soils. The effectiveness of rock phosphate depends on many factors such as particle size of rock phosphate, soil pH and nature of crop. The field experiments conducted to assess the fertilizer value of rock-phosphate in acid soils have shown that although the direct effects was not statistically significant, but the residual effects taken together as judged by grain yield and total phosphorus uptake were significant.

(b) TYPE OF ROCK PHOSPHATE:

Systematic comparisons among Indian rock phosphate are few. Phosphate rocks from Singhbhum and Palamau were about one third as effective as SSP, Purrulia rock, which along with MRP is now widely recommended for soils of pH less than 5.5 has performed equal to MRP in several case. The performance expected on the basis of citrate solubility of rock phosphate does not always seems to hold under field conditions.

(c) GRADE OF ROCK PHOSPHATE:

Being product of nature, composition of rock phosphate has a certain variability. Proportion of citrate soluble P in a given rock can vary from 6% to 26% (Narayanswamy and Sarkar, 1984)

(d) PARTICLE SIZE:

There is a general agreement that material of 60-100 mesh is the best. Citrate soluble P in MRP doubled when its fineness increased from 60 to 100 mesh. In an interesting report on rice in the acid soil of Assam (pH. 5.0), MRP of 100 mesh produced a greater direct response, while the 60 mesh material produced a bigger residual effect. At the end of the cropping cycle both sizes were equally effective.

(e) TIME OF APPLICATION

Efficiency of rock phosphate can be increased if it is mixed with the soil 2-4 weeks ahead of planting both for flooded rice and upland cropping systems. This provides time for the rock to react with the soil and release some P through dissolution before the crop is established.

(f) USE OF ORGANIC MATTER:

It is often reported that application of FYM and other organic materials increases the efficiency of rock phosphate.

Table 2.1 : Typical Analysis of Rock Phosphate (Indegenous Mussoorie Rock Phosphate (PPCL)

Constituents	Percentage
BPL-Grade	44/52
P_2O_5	23.32-24.57
CO_2	10.35-16.22
SiO_3	9.60
CaO	41.0-41.23
SO_2	0.43-1.22
Fe_2O_3	0.40-6.14
Al_2O_3	0.35-0.65
MgO	4.30-4.59
Na_2O	0.09-0.22
K_2O	0.10-0.36
F	1.20-1.38
Cl	0.10

Source : Fertilizer Statistics 1992-93, FAI New Delhi.

REACTION IN SOIL:

When finely ground rock phosphate is applied to acidic soils, containing a high percentage of organic matter, carbonic acid and nitric acid present in the soil act on rock phosphate which contains tricalcium phosphate and convert unavailable phosphate to monocalcium phosphate or water soluble phosphate which is easily available to growing plants. The reactions can be expressed in a simple way as follow:

(i) $[Ca_3\ (Po_4)]\ CaCo_3 + 6H_2CO_3$ = $3\ Ca\ (H_2PO_4)_2 +$ 7Ca CC

(Rock Phosphate containing no flourine) (Carbonic acid) (Monocalcium phosphate) (Calciu carbona

(ii) $[Ca_3(PO_4)_2]_3\ Ca\ Co_3 + 14\ HNO_3 = 3Ca\ (H_2PO_4)_2 + 7\ Ca\ (NO_3)$

(Rock phosphate) (Monocalcium phosphate) (Calcium nitrate)

$+\ H_2CO_3$

(Corbonic acid)

It has been observed that the field crops vary in their ability to utilize phosphorus from rock phosphate. Legumes which have a high calcium requirement appear to respond more to rock phosphate than to non legumes. Field crops can be classified as in Table 2.2, on the basis of their capacity to utilize ground rock phosphate.

Table 2.2 : Classification of field crops in accordance with efficiency in the raw rock phosphate.

Most efficient	Modertley efficient	Least efficient
Turnip	Lucerne	Cotton
Sweet-clover	Peas	Rice
Sarson	Rape	Jowar
(Brassica sp.)	Toria	Barley
		Oats
Spinach		Cabbage

Motsara et al. (1976) observed that the use of MRP in acid soils (pH 4.5-5.4) did not show significant differences between yields obtained under the application of 80,160 and 240 kg/ha. P_2O_5 through rock phosphate. The application of 80 kg/ha P_2O_5 through super phosphate and rock phosphate gave similar yield of paddy, wheat and maize but peas were benefitted more with rock phosphate. On the evaluation of residual effect, it was found that rock phosphate was significantly better than superphosphate, with respect to crop yield and residual P status of the soils. However, potato crop was benefitted more by super phosphate application than by rock phosphate

At Pantnagar, a project on the utilization of Mussoorie rock phosphate was undertaken during the years 1972-74.It was found that Mussoorie rock phosphate could be used for direct application to acid soils. The rate of application should be double the rate of superphosphate on P_2O_5 basis.

Sahu et al. (1974) studied the comparative efficiency of seven rock phosphates of which the only Udaipur one was of Indian origin. These rock phosphates were used for the production of rice crop and were tested for only two seasons. Since this paper reported results of a short term study, better residual effects of rock phosphate as found on long term studies els where, could not be discerned. However, the rock phosphate treatment resulted in much higher yield compared to no phosphate treatment.

Mathur et al. (1979) studied the response of the igneous and sedimentary phosphate rocks of Bihar in acid red loam soil (pH.5.2.) and their residual effect on crop and phosphatic fertility status. Application of 150 kg P_2O_5/ha as phosphate rock could be compared with 50kg P_2O_5 dose as SSP in increasing the yield of crops. Sedimentary phosphate rock (phosphorite) raised the soil pH and available P but igneous phosphate rock

left more residual P in soil.

Misra and Mani (1991) observed that the growth of fenugreek plant and yield of green vegetable matter were considerably increased with increased dose of MRP along with sewage sludge. The synergistic effect of sewage sludge and phosphatic materials may be due to reduced uptake of toxic heavy metals present in the sewage sludge.

M.R.P. has been used as an amendment by Misra and coworkers in order to decrease the availablity of heavy metals to the growing crops in the soil where sludge had been added. As the sewage being used for irrigating vegetable crops is low in P_2O_5, it was considered useful to mix MRP to the soil and irrigate the crops with sewage because MRP can ultimately become available and thus can serve as a ready source of available P to the crops and also can interact with the heavy metals present in the sewage.

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CHAPTER III

CHAPTER - III

MATERIALS AND METHODS (GENERAL):

The experimental works were conducted during the years 1992-1995. The details of materials and methods employed are as follows:

LOCATION OF THE EXPERIMENTAL SITE:

All experiments were conducted at the experimental farm of Sheila Dhar Institute of Soil Science, University of Allahabad. The farm is surrounded by the municipal drains on two sides and domestic waste flows through these drains. These also receive waste from different small cottage industries. The whole farm is being irrigated by municipal sewage water for more than one and a half decade. Mostly seasonal vegetables are grown on this farm.

CLIMATE:

The climate of Allahabad district is tropical. The winter is very cold and summer is intolerable. However, the rainy season is pleasant. The average rainfall in the district is about 82.1 cm per annum, and mean annual temperature varies from 32.4°C to 36.0°C. The humidity stands at about 64%.

CHARACTERISTICS OF THE FARM SOIL:

The Sheila Dhar Institute research farm has alluvial soil (Entisol) and the texture of soil is sandy clay loam. It contains some heavy metals due to sewage irrigation. The chemical analysis of the soil is given in the Table 3.1.

DETAILS OF FIELD EXPERIMENTS:

The experiments were conducted to find out the effects of sewage and Mussoorie rock-phosphate on the uptake of nutrients. The total area taken was 18 m^2 and each microplot was kept uniform ($1m^2$) and lay out was randomized block design having two factors, six treatments and three replications. Layout plan of different treatments is given in the diagram (see separate sheet).

TEST CROPS: Three vegetable crops were taken as test crops (The first crop was taken twice).

1. Fenugreek (*Trigonella foenugraecum*)
2. Spinach (*Spinacia oleracia*)
3. Radish (*Raphanus sativus*)

These crops were grown control sewage irrigated plots and in Mussoorie Rock Phosphate (MRP) treated plots. Five doses of (100, 200, 300, 500 and 700 kg/ha)

of Mussoorie rock phosphate were used. These crops were sown in various seasons in the experimental farm.

BIOMETRIC OBSERVATIONS:

Three plants were selected from each plot. Height of these plants were recorded at 15 days intervals. The number of leaves of the same plants were also noted. When vegetative growth completed and flowering started, crop was pulled out and washed, kept in shade and then weighed for the green biomass.

SOIL SAMPLE COLLECTION:

For chemical analysis of the soil, bulk soil samples (0-15 cm depth) were collected with the help of auger from various plots, mixed and 1 kg of the sample was reserved for the analysis.

SEWAGE SAMPLE COLLECTION:

Sewage waters were collected in one litre polythene bottles from different selected places of drain, and these samples were mixed to get representative sample for analysis of metal and soluble salts.

PREPARATION OF SOIL SAMPLE:

After airdrying, soil samples were crushed gently in pestle and mortar and sieved through a 2 mm. sieve.

Nearly all determinations were carried out on the fractions less than 2 mm. Ground samples were stored in card board andin plastic containers.

A. SOIL ANALYSIS

1. MECHANICAL ANALYSIS:

Mechanical analysis was done by International pipette method as outlined by Piper (1963).

2. pH :

All pH measurements of soil samples were made with pH meter Elico Model L-110, Electronic industrial Co. Pvt. Ltd. Hyderabad, using reference and glass electrode in 1:2.5 (Soil : distilled water) suspension.

3. CATION EXCHANGE CAPACITY:

CEC of soil was determined by the method described by Jackson (1973).

4. ELECTRICAL CONDUCTIVITY (EC) (dSm^{-1}):

EC at 25°C of saturation extract was determined with the help of conductivity bridge as outlined by Jackson (1973).

5. ORGANIC CARBON:

Organic carbon was estimated by the modified

Walkley-Black's method in which known amount of soil sample was oxidized with a known volume of pottassium dichromate ($K_2Cr_2O_7$) and concentrated H_2SO_4 utilizing the heat of dilution of H_2SO_4. Unused $K_2Cr_2O_7$ was back-titrated with ferrous sulphate ($FeSO_4 \cdot 7H_2O$ or $FeSO_4\ (NH_4)_2\ SO_4\ 6H_2O$).

$$\text{Organic Carbon (\%)} = \frac{10(B-T)}{B} \times \frac{0.003 \times 100}{\text{Wt. of soil (g)}}$$

Where B = Volume (ml.) of ferrous (ammonium) sulphate solution required for blank titration.

T = Volume of ferrous (ammonium) sulphate solution needed for titration of soil sample.

Organic matter (%) = Actual C (%) X 1.724.

The Van Bemmelen factor of 1.724 is used because organic matter contains 58% C.

NITROGEN :

Available N was estimated by the method described by Jackson (1973).

PHOSPHORUS:

Available P was determined by Olsen's method (Olsen et al. 1954) (using 0.5M $Na\cancel{C}HO_3$ adjusted to, pH 8.5 with the help by spectrophotometer, Spectronic 21-D model DUV-Digital read out and UV/Visible

wavelength).

$$\text{Available P (kg/ha)} = \frac{\text{R x volume of extract}}{\text{Volume of aliquot}} \times \frac{2.24 \times 10^6}{\text{Wt.(g) of soils} \times 10^6}$$

Where R = μ g P in the aliquot (obatain from standard curve)

$$\frac{R \times 50 \times 2.24}{5 \times 2.5} = \mu \text{g P} \times 8.96$$

POTTASIUM:

Available K of soil sample was determined by Flame photometer method described by Jackson (1973).

ANALYSIS OF HEAVY METALS IN SOIL:

Lindsay and Norvell (1978) developed a method using DTPA (Diethylene Triamine Penta-Acetic Acid) which was found useful for separating soils in deficient and non-deficient categories for Zn, Cu, Mn and Fe by using atomic absorption spectrophotometer.

PREPARATION OF DTPA SOLUTION:

Reagents:

1. DTPA (Diethyline Triamine Penta - Acetic Acid)
2. TEA (Triethylene amine) 0.1M (A.R.)
3. $CaCl_2$ $2H_2O$ 0.1M sol. (A.R.)

4. Dilute HCl. (A.R. HCl diluted with double distilled water 1:5).

To prepare 1 litre of DTPA extracting solution 13.1 ml reagent grade TEA, 1.967 g DTPA (A.R.) and 1.47 g of $CaCl_2$ were dissoloved in 100 ml of glass distilled water. DTPA was allowed to dissolve and diluted to approximately 900 ml, was adjusted pH to 7.3$\pm$.05 with 1:1 HCl while stirring and then diluted to 1 litre. Addition of approximately 4 ml of 1N HCl brought the pH of the solution to 7.3 (This solution is stable for several months).

EXTRACTION AND DETERMINATION:

10 grams of air dried soil was weighed in a 125ml. conical flask or polypropylene bottle. Then 20 ml of DTPA extracting sotution was added. The bottles of flask were corked and placed upright on a horizontal shaker. These were shaken for two hours with a speed of 120 cycle per minute. Suspension was filtered through Whatman no. 42 filter paper. The filtrate was kept in polypropylene bottle to be analysed for Zn, Cu, Cr, Fe and Pb with Atomic absorption spectrophotometer. When samples needed dilution before measurement, they were diluted with DTPA solution to maintain a constant matrix.

Experimental conditions such as shaking time, DTPA concentration, pH and temperature during shaking influence the amount of Zn, Cu, and Fe extracted by DTPA. The most suitable pH of extracting solution is 7.3, shaking time 2 hours and temperature during shaking 25 ± 1°C. (The values of the nutrient extracted will change if these precautions are not followed. Increase in shaking time and temperature markedly enhance the extractability of Zn, Cu, Pb, Cr and Fe).

DETERMINATION OF TOTAL HEAVY METALS IN SOIL:

Di-acid digestion:

It was carried out using a 9:4 mixture of HNO_3 and $HClO_4$.

One g. ground plant material was placed in 100 ml volumetric flask. To this 10 ml of acid mixture was added and the content of the flask were mixed by swirling. The flask was placed on low heat hot plate in a digestion chamber. Then, the flask was heated at higher temperature until the production of red NO_2 fumes ceased. The contents were further evaporated until the volume reduced to about 3-5 ml but not to dryness. The completion of digestion was confirmed, when the liquid become colourless.

After cooling the flask 20 ml of deionized or glass distilled water was added, volume was made up with deionized water and the solution was filtered through Whatman No.1 filter paper. This soultion was used for the determination of Cu, Cr, Zn, Pb and Fe by the help of A.A.S.

PLANT ANALYSIS:

Preparation of sample:

After harvesting, plants were collected and washed with deionised water and then dried in an oven. Dried plant material was ground and digested in triacid mixture for heavy metals analysis.

Tri acid digestion:

Digestion was carried out using a 5:2:1 mixture of HNO_3 conc. $HClO_4$ and conc. H_2SO_4.

One g. of ground plant material was placed in 100 ml of beaker, and 10 ml triacid mixture was added. The contents were heated on a hot plate at low heat for 30 minutes and the volume was reduced to about 5 ml.

After cooling the beaker, 20 ml of distilled water was added and contents filtered through filter paper (Whatman No. 42) into a 100 ml of volumetric flask and

the volume was made up with distilled water.

Heavy metals in plants samples were determined directly using A.A.S.

HEAVY METALS DETECTION IN SEWAGE:

Metals have a tendency to form complexes readily with the organic constituents, hence it is necessary to destroy them by digestion with strong acid. The preliminary acid-digestion not only destroys organic matter but also brings all suspended metallic compounds into solution.

DIGESTION WITH NITRIC AND SULPHURIC ACID:

For the estimation of heavy metals, nitric acid digestion was adopted. 100 ml. sewage sample was taken in a 250 ml. of beaker and 5 ml conc. HNO_3 was added. The mixture was brought a slow boil and then evaporated on a hot plate to the lowest volume (15-20 ml.). To the remaining portion, 5 ml conc. HNO_3 was again added and the contents heated to a gentle refluxing action. The contents were cooled and walls of the beaker were washed down and then contents filtered. The filtrate was taken in a 100 ml. volumetric flask and mixed throughly. 1 ml. of digested solution was taken for each metal to be detected with the help of AAS. The

chemical analysis of the sewage is given in Table 3.2

ATOMIC ABSORPTION SPECTROPHOTOMETER (AAS):

Principle:

The AAS is based on the principle that atoms of metallic elements (Fe, Mn, Cu, Zn, Cr, Pb etc.), which normally remain in ground state under flame conditions absorb energy when subjected to radiation of specific wavelength. The absorption of radiation is proportional to the concentration of atoms of that element. The absorption of radiation by the atoms is independent of the wavelength of absorption and temperature of the atoms. These two features provide AAS a distinct advantage over flame emission spectroscopy. It also has greater sensitivity and accuracy.

INSTRUMENTATION:

A double beam atomic absorption spectrophotometer is required. The two most common oxidant/fuel combination used in atomic absorption spectroscopy are air-acetylyne and nitrous oxide-acetylene. Other flames that can be used are air hydrogen and argon-hydrogen entrained air.

Air acetylene is the preferred flame for the determination of approximately 35 elements by atomic

absorption. The temperature ranges from 2125-2400°C.

Nitrous-acetylene flame has a temperature ranging from 2600-2800°C and is used for the determination of elements which form refractory oxides. It is also used to overcome chemical interferences that may be present in flames of lower temperature. However, light emission from the nitrous oxide-acetylene flames is very strong for certain wavelengths. This may cause fluctuations in the analytical results for determination performed at these wavelengths, particularly if the lamp emission for the element of interest is weak. Only the nitrous oxide burner head can be used with the nitrous oxide-acetylene flame.

STATISTICAL ANALYSIS:

Correlation studies were made between sewage and heavy metals content, Sewage and plant height and biomass, and Mussoorie rock phosphate and heavy metals. These were calculated by the formula given in the book entitled Statistical Methods for Agricultural Workers (Panse and Sukhatme 1963).

In discussing the results, depending on the value of correlation coefficient (r), results have been reported as mildlyor strongly correlated.

Table 3.1 : Physico-chemical properties of SDI experimental farm soil (Before experiments)

Properties			
pH			7.3
EC (d Sm^{-1}) at 25°C)			0.48
CEC (C mol (p^{+}) kg^{-1})			21.5
Organic Carbon (%)			1.0
Organic Matter (%)			1.732
Nitrogen (%)			0.14
Potash (kg/ha)			238
Phosphorus (kg/ha)			9.0
DPTA extractable	Zn	(ppm)	9.9
	Cu	(ppm)	6.0
	Fe	(ppm)	20.2
	Cr	(ppm)	2.9
	Pb	(ppm)	5.6

Table 3.2 : Physico-chemical properties of SDI experimental farm sewage water.

Properties		
pH	7.0	7.5
EC (dSm^{-1})	910	2015
Total solids (mg/l)	180	390
Chloride (mg/l)	15.0	30.0
Total Nitrogen (mg/l)	2.10	7.39
Nitrate nitrogen (mg/l)	0.03	0.081
Phosphate (mg/l)	0.04	1.2
Sulphate (mg/l)	5.1	13.3
Zn (ppm)	11.4	
Cr (ppm)	2.9	
Cu (ppm)	9.0	
Pb (ppm)	8.4	
Fe (ppm)	28.3	

Table 3.3 : Phosphorus determination of soil after first crop.

Treatments	P_2O_5 (kg/ha)
T_0 S (Control)	9.90
T_1 S (100 kg MRP/ha)	13.50
T_2 S (200 kg MRP/ha)	15.00
T_3 S (300 kg MRP/ha)	18.10
T_4 S (500 kg MRP/ha)	26.80
T_5 S (700 kg MRP/ha)	29.95

Table 3.4: Residual phosphate determination of soil after second crop.

Treatments	P_2O_5 (kg/ha)
R_0 S (Control)	10.00
R_1 S (100 kg MRP/ha)	14.80
R_2 S (200 kg MRP/ha)	16.50
R_3 S (300 kg MRP/ha)	20.95
R_4 S (500 kg MRP/ha)	28.10
R_5 S (700 kg MRP/ha)	31.10

Table 3.5 : Phosphorus determination of soil after third crop.

Treatments	P_2O_5 (kg/ha)
P_0 S (Control)	9.10
P_1 S (100 kg MRP/ha)	17.80
P_2 S (200 kg MRP/ha)	24.00
P_3 S (300 kg MRP/ha)	29.85
P_4 S (500 kg MRP/ha)	35.21
P_5 S (700 kg MRP/ha)	39.00

Table 3.6 : Phosphorus determination of soil after fourth crop.

Treatments	P_2O_5 (kg/ha)
T_0 (Control)	9.90
T_1 (100 kg MRP/ha)	19.10
T_2 (200 kg MRP/ha)	27.80
T_3 (300 kg MRP/ha)	36.15
T_4 (500 kg MRP/ha)	43.20
T_5 (700 kg MRP/ha)	52.00

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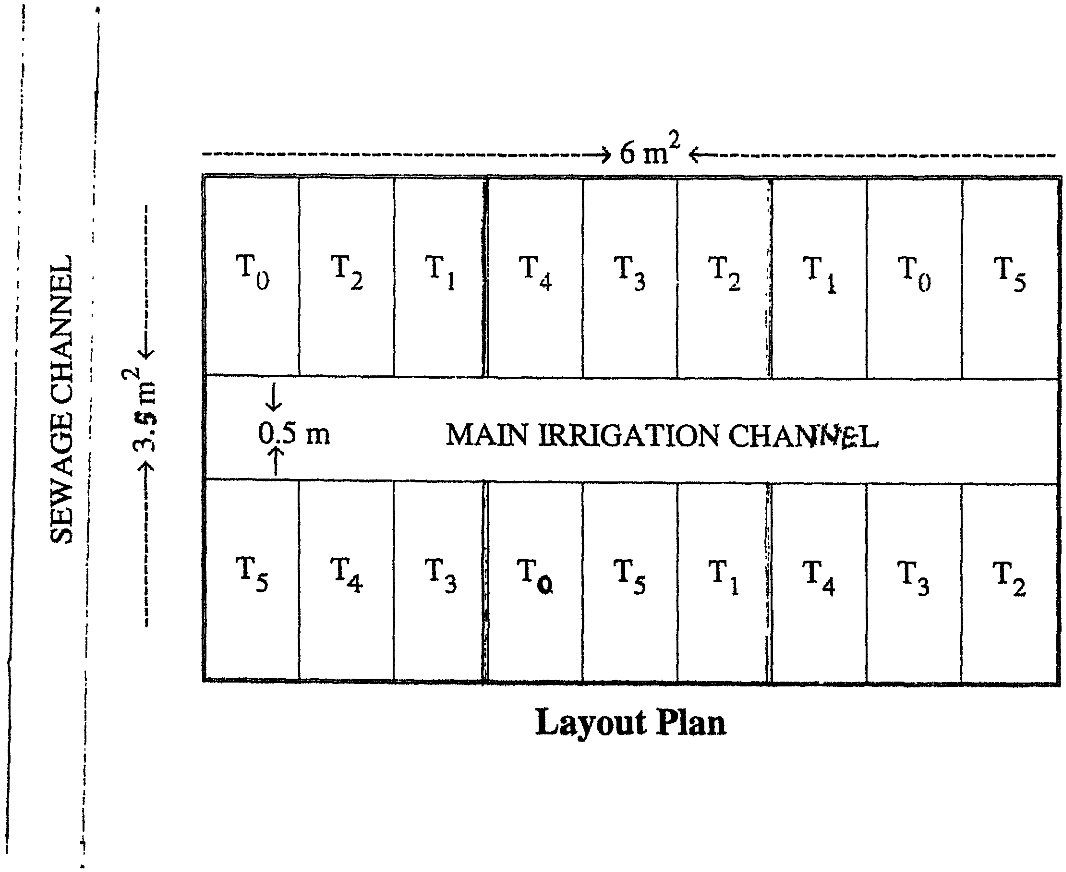
SEWAGE CHANNEL
6 m2
3.5 m2
0.5 m
MAIN IRRIGATION CHANNEL
T0
T2
T1
T4
T3
T2
T1
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T5
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T4
T3
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T2

Layout Plan

CHAPTER IV

CHAPTER - IV

EFFECT OF SEWAGE AND MUSSOORIE ROCK-PHOSPHATE ON THE BIOMETRIC PARAMETERS:

Nutrients and water being major constraints in the development of Indian agriculture, harvesting the nutrient energy of biological and industrial wastes is of prime importance for maximising the food, feed, fodder and fuel production in the country.

The ideal management practices on sewage farms call for application of waste water only in such volumes as suit the needs of the crops being raised. Ignorance about the nutrient composition of waste water further aggravates the imbalance in the contents of various plant nutrients. Sewage farming can be effectively followed for soils, affected by drought and the consequential moisture stress conditions.

Metcalf and Eddy (1916) found the efficacy of sewage in supplying the requisite manurial values for crop growing. The manurial value of sewage is far less than commonly supposed on account of the great dilution of the constituents serviceable to plant life, nitrogen, phosphorus and potash.

Kardos (1967) found that hay yields were increased by 139 per cent, corn grain 78 per cent and oat grain 70 per cent due to use of sewage effluents.

Norwell and Sawhney (1974), Cunninghum et al.(1975) and Giordano et al. (1975) have reported accelerated maize growth and yield in sewage sludge ammended soils.

Chhabra (1988) reported that sewage water contains large quantities of plant nutrients. A survey of major towns of Haryana has shown that these waters, in addition to meeting water requirement, add about 36.2, 5.7 , 54.0 and 15.6 kg of N.P.K and S respectively in one application when used for irrigation. However considering the social attitude, odour, hazards due to pathogen, soluble organic compounds, toxic elements (Pb, Cd and Ni) and their large volumes near the cities, only 10 to 50% of these waters are being utilised while the rest are causing serious river and land pollution.

Misra and Mani (1990) observed that the growth of fenugreek plant and the yield of greeny vegetable matter were considerably increased with the increased dose of Mussoorie rock phosphate alongwith

sewage/sludge.

Gupta et al. (1993) reported that grain and straw yield of wheat increased with the application of sewage sludge and phosphate. The interaction of sewage sludge and phosphate on the grain yield of wheat was not significant. Total phosphate and nitrogen uptake by wheat increased with the increased application of sewage sludge and phosphate. Organic carbon content and Olsen's extractable P of post harvest soil samples increased with the application of sewage sludge. But phosphate application increased only Olsen's P and soil carbon remained unaffected.

Misra and Kumar (1994) found that fenugreek growth and yield increased with increasing application of sewage sludge alongwith MRP (Mussoorie rock phosphate). The application of sewage sludge alongwith 1000 kg MRP/ha, gave 12.72% excess biomass in comparison to the control.

However application of fertilizer to the sewage irrigated crops brought about considerable increase in yield. The response of crop yield to the application of recommended dose of NPK to sewage irrigated crop was not much different from that recorded on the

application of supplemental NPK through fertilizer in addition to those contributed by sewage so as to make up the deficiency, if any, from recommended level of major nutrients for crops.

From the review, it is clear that there is a good response of added P to sewage irrigated soils, hence Mussoorie rock phosphate was tried as a source of slowly available P in order to improve the quality of sewage through P amendment.

EXPERIMENTAL DETAIL:

The field experiments were conducted at Sheila Dhar Institute Research farm, Allahabad. The size of the each plot was $1m^2$ and randomized block design (RBD) was adopted.

The experimental field was chosen near sewage water drain. The treatments consisted of 5 doses of MRP and sewage was used for irrigating the crops.

EXPERIMENT-I:

Experiment with Fenugreek (Trigonelles foenumgraecum):

The area of experimental plot was $18m^2$, and the size of each microplot was $1m^2$. The two factors (sewage and MRP) were combined into 6 treatments and

replicated thrice. MRP was applied at 5 levels @ 100, 200, 300, 500 and 700 kg/ha, 20 days before sowing the test crop. The sowing was done on 20 October 1992 at the rate of 30 kg/ha. Experimental plots were irrigated with sewage water. The height of crop was recorded at 15 days interval. The crop was uprooted after 60 days of sowing. Leaf and root biomass was recorded separately. The data regarding growth and yield are given Tables 4.1 and 4.4 respectively.

Treatments :

1. T_0 S (Sewage + MRP 0)
2. T_1 S (Sewage + MRP 100 kg/ha)
3. T_2 S (Sewage + MRP 200 kg/ha)
4. T_3 S (Sewage + MRP 300 kg/ha)
5. T_4 S (Sewage + MRP 500 kg/ha)
6. T_5 S (Sewage + MRP 700 kg/ha)

Table 4.1 : Average height of plants (cm)

Treatments	Days			
	15	30	45	60
T_0 S	6	8	18	28
T_1 S	6	14	26	29
T_2 S	6	16	27	32
T_3 S	7	18	29	36
T_4 S	8	18	32	38
T_5 S	8	19	34	39
	r=0.39	r=0.68	r=0.73	r=0.93

Table 4.2 : Total biomass of the crop (g)

Treatments	Weight
T_0 S	1240
T_1 S	1560
T_2 S	1600
T_3 S	1700
T_4 S	1710
T_5 S	1890
	r=0.93

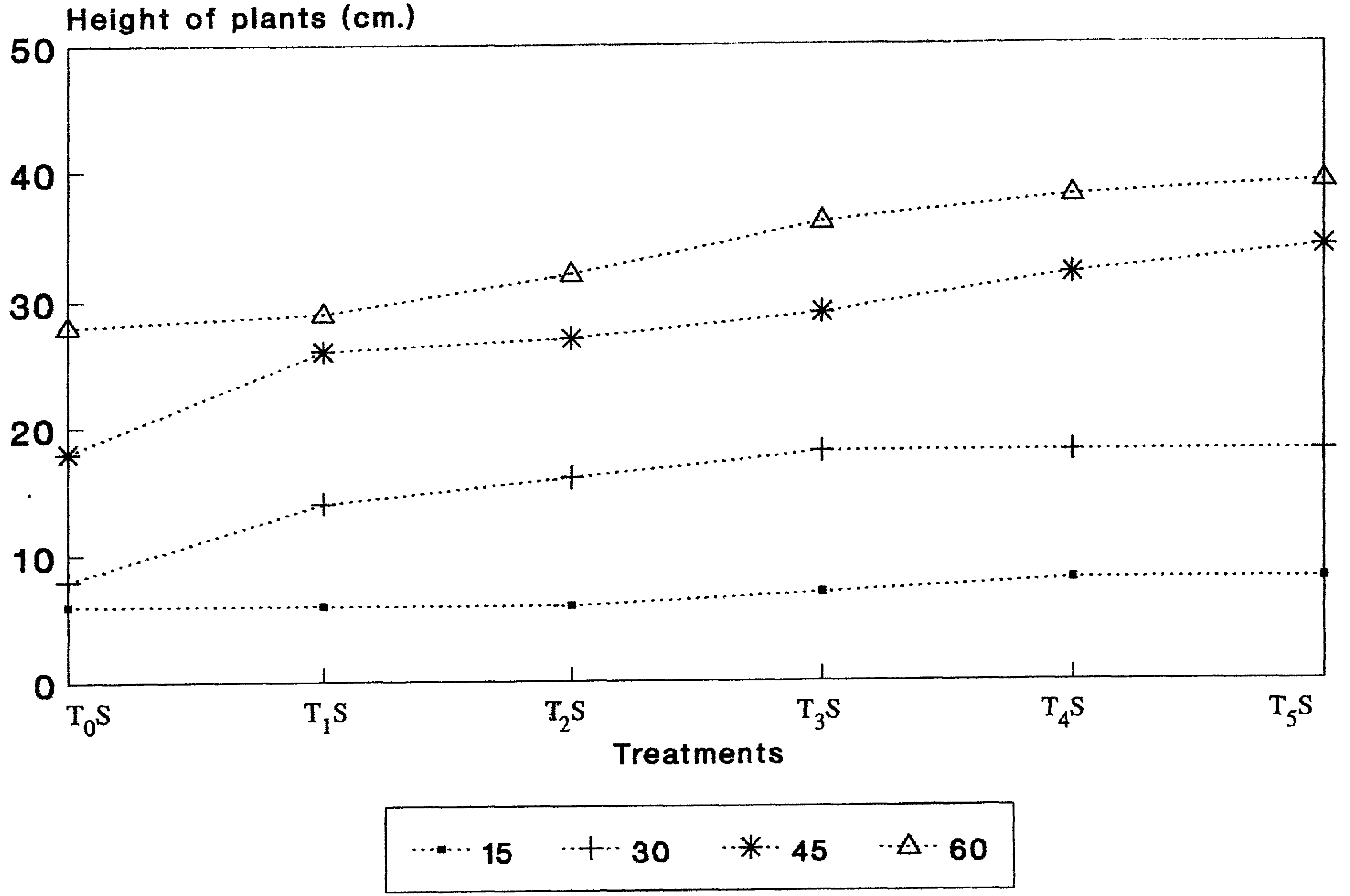

Fig. 4.1 Average height of Fenugreek plants

Table 4.3 : Fresh biomass of leaves (g)

Treatments	Weight
T_0 S	1110
T_1 S	1360
T_2 S	1400
T_3 S	1490
T_4 S	1495
T_5 S	1640

r=0.73

Table 4.4 : Fresh biomass of the roots (g)

Treatments	Weight
T_0 S	130
T_1 S	200
T_2 S	200
T_3 S	210
T_4 S	215
T_5 S	250

r=0.70

EXPERIMENT-II :

Experiment with spinach (*Spinacia oleracea*):

The field experiment was conducted at the same plots in order determine the residual effect of MRP of previous the experiment. Spinach was grown as a test crop in the microplots. The sowing was done on 10th January 1993 at the rate of 20 kg/ha.

Treatments:

1.	R_0 S	(Sewage + MRP 0)
2.	R_1 S	(Sewage + MRP 100 kg/ha)
3.	R_2 S	(Sewage + MRP 200 kg/ha)
4.	R_3 S	(Sewage + MRP 300 kg/ha)
5.	R_4 S	(Sewage + MRP 500 kg/ha)
6.	R_5 S	(Sewage + MRP 700 kg/ha)

Spinach crop was irrigated with sewage water. The height of plants was measured after 15 days intervals. The biomass was determined after 60 days by uprooting the crop.

The data regarding growth and yield are given Tables 4.5 to 4.8.

Table 4.5 : Average height of plants (cm).

Treatments	Days			
	15	30	45	60
R_0 S	6	11	15	25
R_1 S	6	16	24	28
R_2 S	7	21	27	30
R_3 S	9	25	30	31
R_4 S	9	26	31	33
R_5 S	10	27	32	36
	r=0.37	r=0.86	r=0.82	r=0.82

Table 4.6 : Total Biomass of the Crop (g)

Treatments	Weight
R_0 S	1440
R_1 S	1950
R_2 S	2090
R_3 S	2210
R_4 S	2630
R_5 S	2990
	r = 0.99

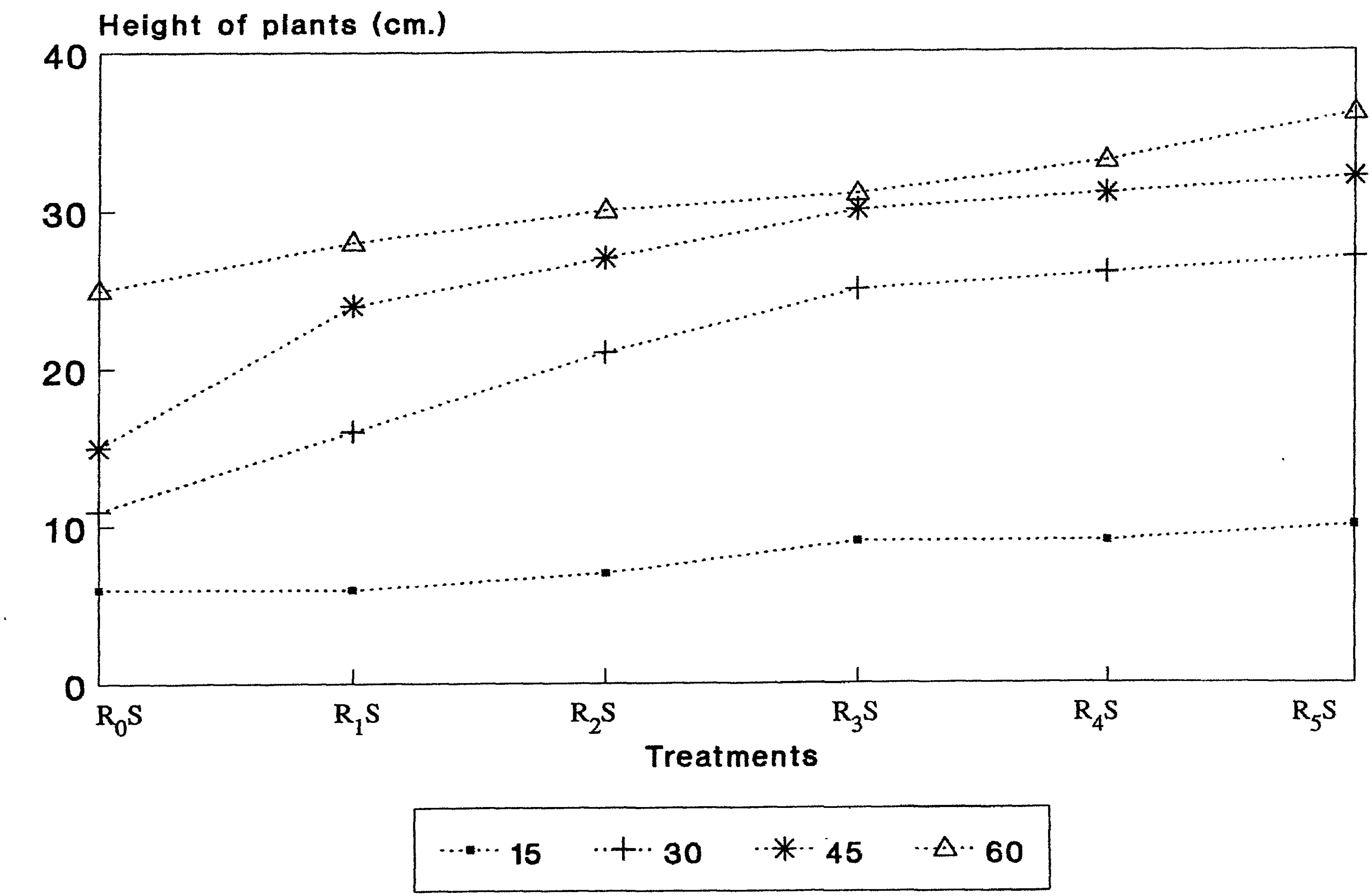

Fig. 4.5 Average height of Spinach plants

Table 4.7 : Fresh Biomass of the crop leaves (g)

Treatments	Weight
R_0 S	1280
R_1 S	1790
R_2 S	1890
R_3 S	2000
R_4 S	2300
R_5 S	2650

$r = 0.75$

Table 4.8 : Fresh Biomass of the crop roots (g)

Treatments	Weight
R_0 S	160
R_1 S	160
R_2 S	200
R_3 S	210
R_4 S	330
R_5 S	340

$r = 0.72$

EXPERIMENT III

Experiment with Fenugreek.

The experiment was conducted in the same microplots in order to find out the effect of different doses of Mussoorie rock phosphate on the growth and yield of fenugreek.

Treatments:

1.	P_0 S	(MRP 0 + Sewage)
2.	P_1 S	(MRP 100 kg/ha + Sewage)
3.	P_2 S	(MRP 200 kg/ha + Sewage)
4.	P_3 S	(MRP 300 kg/ha + Sewage)
5.	P_4 S	(MRP 500 kg/ha + Sewage)
6.	P_5 S	(MRP 700 kg/ha + Sewage)

The crop was sown on 15th October 1993 and it was irrigated with sewage water. MRP was applied 20 days before sowing the test crop. Seed rate was 30 Kg/ha.

The height of test crop was recorded at 15 days interval. The crop was uprooted after 60 days of sowing. The total biomass was recorded separately for shoots and root.

The data regarding growth and yield are given in Tables 4.9 to 4.12

Table 4.9 : Average height of plants (cm).

Treatments	Days			
	15	30	45	60
P_0 S	5	10	17	29
P_1 S	6	14	20	31
P_2 S	6	16	25	33
P_3 S	7	20	29	34
P_4 S	9	27	30	36
P_5 S	9	28	32	38
	r=0.43	r=0.98	r=0.93	r=0.92

Table 4.10 : Total Biomas of the crop (g)

Treatments	Weight
P_0 S	1360
P_1 S	1440
P_2 S	1500
P_3 S	1520
P_4 S	1625
P_5 S	1910
	r = 0.91

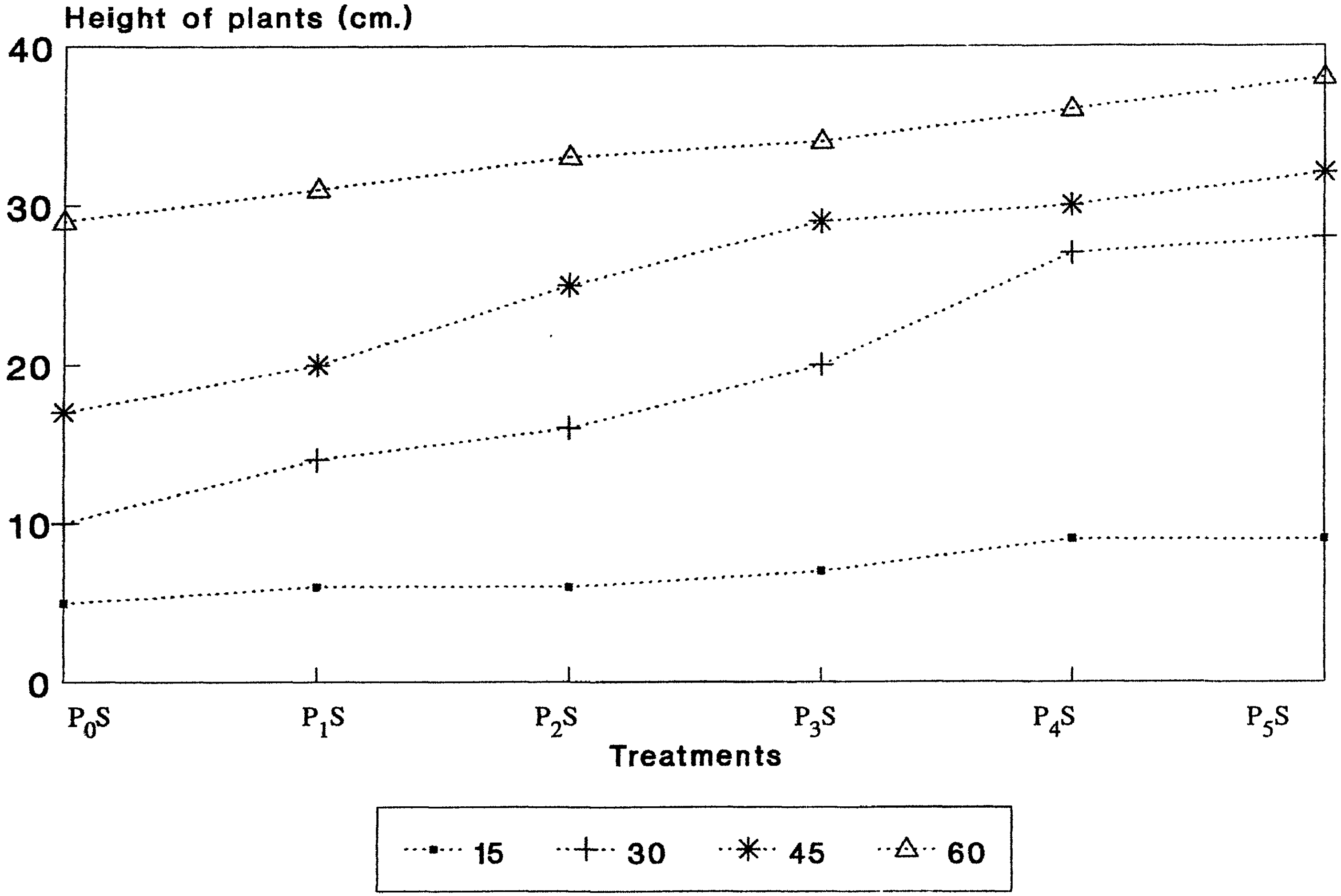

Fig. 4.9 Average height of Fenugreek plants

Table 4.11 : Fresh Biomass of the leaves (g.)

Treatments	Weight
P_0 S	1210
P_1 S	1280
P_2 S	1300
P_3 S	1310
P_4 S	1405
P_5 S	1675

$r = 0.72$

Table 4.12 : Fresh Biomass of the roots (g.)

Treatments	Weight
P_0 S	150
P_1 S	160
P_2 S	200
P_3 S	210
P_4 S	220
P_5 S	235

$r = 0.92$

EXPERIMENT-IV

Experiment with Radish (Raphanus sativus):

This experiment was also conducted at Sheila Dhar Institute farm. The two factors (sewage and MRP) were combined into six treatments and replicated thrice. MRP was applied again at 5 doses, @ 100,200,300,500 and 700 kg/ha. respectively. The MRP was applied 20 days before sowing of the test crop.

The sowing was done on 15th January 1994 at the rate of 12 kg/ha. The test crop was irrigated with sewage water.

Treatments:

T_0 (MRP 0 + Sewage)

T_1 (MRP 100 kg/ha + Sewage)

T_2 (MRP 200 kg/ha + Sewage)

T_3 (MRP 300 kg/ha + Sewage)

T_4 (MRP 500 kg/ha + Sewage)

T_5 (MRP 700 kg/ha + Sewage)

The height of test crop was recorded after 15 days interval. The biomass was recorded after 60 days by uprooting the crop.

The data regarding height and yield are given in Tables 4.13 to 4.16 .

Table 4.13 : Average height of plants (cm.)

Treatments	Days			
	15	30	45	60
T_0	8	11	19	29
T_1	8	15	24	32
T_2	9	20	29	35
T_3	10	24	30	35
T_4	10	26	32	37
T_5	12	28	35	38
	r=0.46	r=0.93	r=0.92	r=0.92

Table 4.14 : Total Biomass of the crop (g.)

Treatments	Weight
T_0	1700
T_1	1900
T_2	1990
T_3	2080
T_4	2120
T_5	2200
	r=0.93

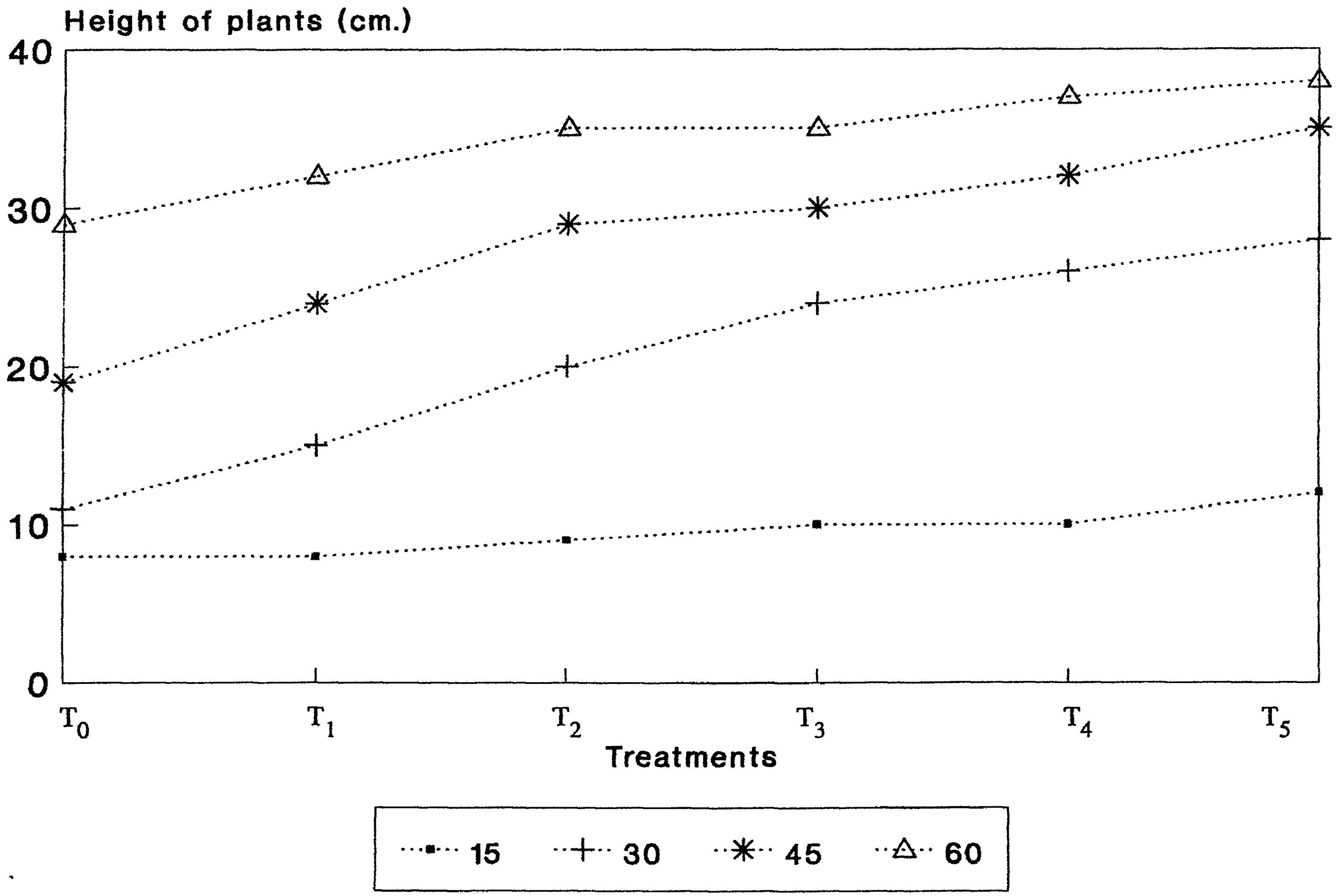

Fig. 4.13 Average height of Radish plants

Table 4.15 : Fresh Biomass of the roots (g.)

Treatment	Weight
T_0	900
T_1	1000
T_2	1080
T_3	1100
T_4	1130
T_5	1200

$r = 0.86$

Table 4.16 : Fresh Biomass of leaves (g.)

Treatments	Weight
T_0	800
T_1	900
T_2	910
T_3	980
T_4	990
T_5	1000

$r = 0.80$

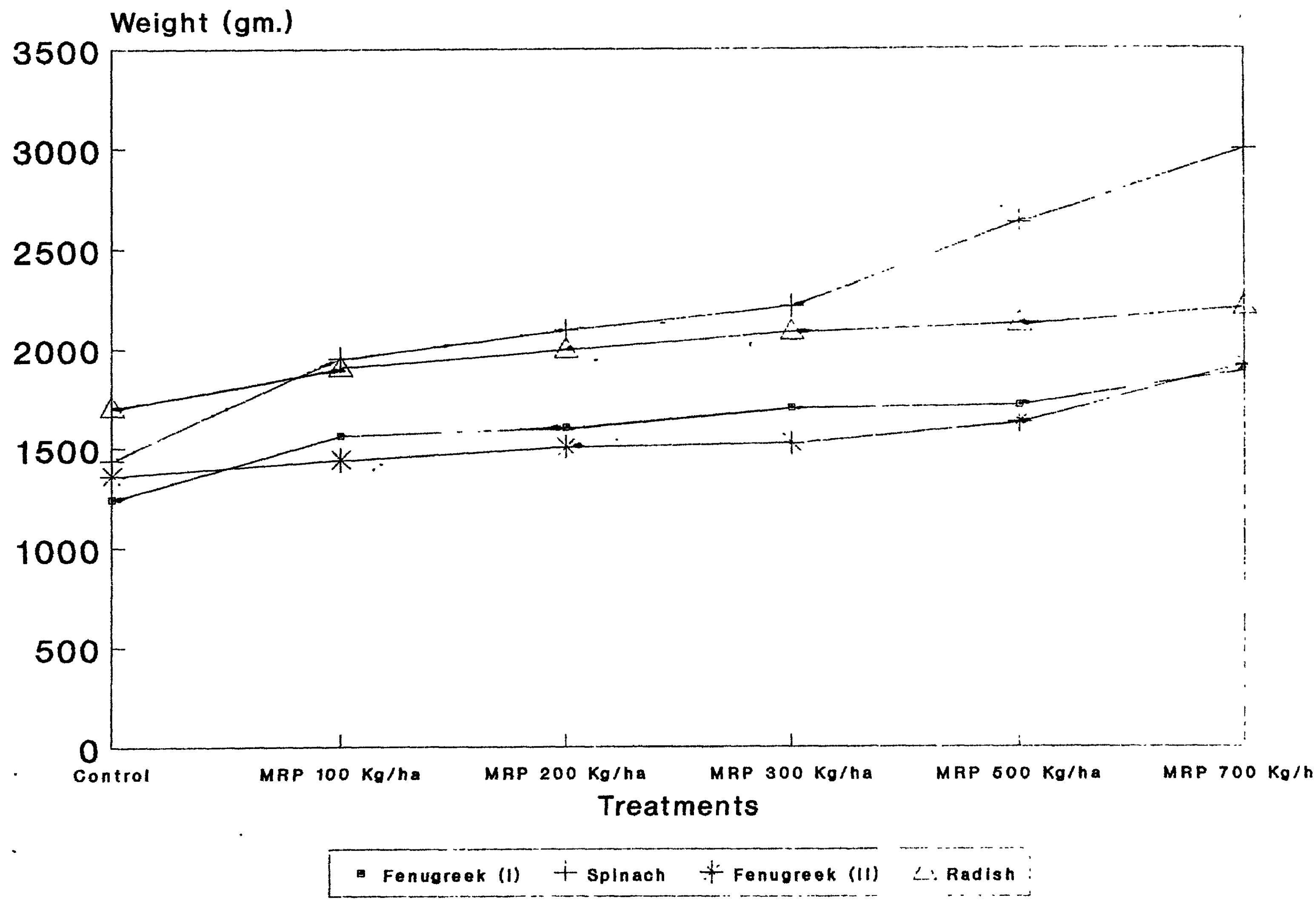

Fig. 4.2, Total biomass of the crop
4.6,

RESULTS AND DISCUSSION:

Height of plants :

From the data regarding growth and yield of four vegetable crops (fenugreek, spinach, fenugreek, radish) it is observed that there is no harmful effect of sewage and Mussoorie rock phosphate on their vegetative growth. Addition of 700 kg MRP/ha resulted in 50% increase in height.

The result on the growth of spinach exhibit the residual effect of MRP. It is found that growth of spinach (Table 4.5) is highest (36 cm.), where 700 kg MRP/ha is added and sewage water is used for irrigation of the crop. In other crops too, there was residual effect of MRP.

In the experiment III MRP was again added. The height of fenugreek plants increased gradually with time. After 15 days of sowing, no remarkable effect was observed on the average height of the plants in different treatments but after 30 days of sowing, the average height of fenugreek plants increased significantly ($r = .098$).

In experiment IV MRP was again added. Thé height of radish increased with different doses of MRP as

compared to sewage irrigated plot. But the increases are not very prominent. Maximum height was found with higher dose of MRP and sewage. From the above,it is clear that the height of different crop plants increased due to inclusion of MRP.

Biomass of plants :

Data given in tables 4.2 & 4.3 show that the biomass of fenugreek increased with the addition of increasing doses of MRP over control. The highest biomass (1890 g) was recorded in T_5S (700 kg/ha.MRP + Sewage water) which is 14% over control plot (only sewage). These results are in close conformity with the findings of Gupta et. al.(1993). Misra and Mani (1991) have also reported that the yield of greeny vegetable matter considerably increased with increased doses of MRP alongwith sewage.

The yield of spinach with highest dose of MRP alongwith sewage water gave the maximum yield (2990g). It shows the residual effect of MRP on the succeeding crop.

From experiment III, it is clear that maximum yield (1910 g.) of fenugreek is obtained in treatment P_5S (700 kg/ha.MRP) which is 550 g. more than the

control.

These results are in close conformity with the report of FAO (1992).

In experiment IV with radish, the yield was better than with other crops. The growth of roots was vigorous with higher dose of MRP. The weight of shoots were more than roots. The maximum yield (2200 g) was found in T_5 (MRP 700 kg/ha) and in control plot (only sewage) the yield was lowest (1700 g).

Thus addition of MRP to sewage greatly increased the value of sewage irrigation which is reflected through increased growth and biomass.

* * * * *

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CHAPTER V

CHAPTER - V

EFFECT OF SEWAGE AND MUSSOORIE ROCK PHOSPHATE ON THE UPTAKE OF HEAVY METALS:

The uptake of ions has been the subject of many and diverse investigations based both on solutions and on the soil. Studies of the mechanism of absorption from solution have been mainly concerned with the macronutrients, but from the limited information on heavy metal ions it seems likely that the mechanisms are similar.

The relative importance of mass flow and diffusion has created some controversy among soil scientists interested in the uptake of ions by plants. No simple answer appears to be applicable to all types of ions, and the processes can generally be regarded as additive, with one or the other being dominant in a particular case depending upon water regime and the sorption characteristics of both root and soil with the heavy metal ions which are firmly held on the adsorbing complex. Other processes may be involved in the immediate vicinity of the roots. The roots and associated microorganisms produce various organic chelating agents which are very effective in releasing

heavy metals from the soil colloid. This would probably mean that greater diffusion gradients are established between the bulk solution and the concentration at the absorbing root.

The characteristics and behaviour of an individual plant species or variety are important in determining the amounts of heavy metals that are taken up from soils. There are few reports of differing rates of absorption (of Zn^{2+} and Mn^{2+}) between species and varieties. Many comparisons have, however, been made between the content of individual heavy metals in the shoots of soil grown plants and these often show wide differences both between species and varieties. Although such differences may reflect differing rates of absorption they will also be dependent on the extent of transport from root to shoots.

The essential macro and micro nutrients are present in the sewage sludge and hence they reach the soil, when sewage irrigation is practised. The addition of trace metals by means of effluent irrigation can be benificial under certain circumstances. However, the main concern today is the danger of accumulation of excessive level of trace elements leading to toxicity and hence to health and environmental hazards.

Much research work has been carried out to obtain reliable information on trace elements uptake and accumulation in plants grown in effluent or sewage sludge treated soils (Page 1974, Bouwer and Chaney 1974, CAST 1976, Chang et al. 1981, Page et al. 1981 Logan and Chaney 1983, Purvis 1985 and Tiller 1989).

In adition to the information on plant response to trace elements and their accumulation in plant tissues obtained for raw sewage amended soils, laboratory studied have been carried out on solution and simulated effluent rich in trace elements. Accumulation of trace elements in plant tissues may detrimentlly affect cropgrowth but some trace metals accumulate in plant meterial without any external signs. Consumption of such materials through the food chain may adversely affect animals and human. Much attention has been paid to Zn, Cd and Pb due to toxicity hazard and their potential for accumulating in plant tissue. Other elements considered as most hazardous due to their occurrence in large quantities in wastes such as sewage sludge and their toxicity affects are Cr, Cu, Ni and Mo.

Raw sewage and sludge depending upon their

sources, may contain an appreciable amount of metallic micronutrients and toxic heavy metals. Long term application of these meterials to cultivated lands may cause accumulation of heavy metals in soil and may become toxic to plants.

The soil chemistry of chromium is poorly understood. It has been reported that when solution of Cr (VI) as potassium chromate were added to soils of pH 4.7 to 7.4, the chromium was rapidly converted to insoluble forms which had properties of a mixed hydrous oxide of Cr (III) and Fe (III) (Cary 1977). It has been suggested that the reduction depends on the presence of organic compounds as electron donors (Grove et al. 1980). Cr (III) appears to be the stable form in the soil solution although present at very low concentrations. Thus although Cr (VI) is much more toxic to plants than Cr (III), it will be reduced to Cr (III) after addition to aerobic soils. The rate of reduction is slower in alkaline than in acid soils, but even in alkaline soils Cr (VI) will be reduced to insoluble forms of Cr (III) within one season (Cary et al. 1977). The mechanism involved in the uptake and translocation of Cr in plants are not understood

largely because of uncertainty about the ionic species present in different systems. There is however, evidence that Cr (VI) is reduced to Cr (III) between the root surface and the shoots and irrespective of the form in which it is supplied.

Cr has occasionally aroused interest as being possibly responsible for the poor growth of plant on serpentine soils, but this seems to be related to chromate in primary minerals, not to trivalent Cr.

Common levels of Cr found in plant material are usually in the range of 0.02 to 0.2 ppm. However, a relatively great variation is observed in the Cr content of food plants (Cary et al. 1977).

The Cr content in plants is controlled mainly by the soluble Cr content of the soils. The ready conversion of soluble Cr^{6+} to insoluble Cr^{3+} under normal soil conditions is of great importance because it is responsible for low Cr availability to plants.

Misra and Jaiswal (1982) reported that at higher level of Cr^{6+} (>25 ppm) the germination of spinach seeds was completly inhibited.

Two pathways are available for Pb to enter plants uptake by the roots and foliage. Once Pb gets inside the system is seems to be enriched in cell membranes, mitochondria and chloroplast.

Under conditions of phosphate sufficiency Pb precipitates as lead phosphate which decreases the uptake of lead and other micronutrients (Machlean et al. 1969, Miller and Koeppe 1970, Cox and Rains 1971).

Organic matter interacts with metal ions contained in the soil forming complex compounds such as amino, hydroxyl, corboxyl and keto groups. The complex compounds formed between organic substances and Pb content of plants assist to translocate Pb. Hence its uptake increases only due to formation of stable complexes with humic and fulvic acids. Thus, organic matter plays a significant role in the solubilization and transport of Pb ions to plants.

Lead reacts with many soil constituents such as clay, phosphate, carbonate, hydroxide, sesquioxides and organic matter resulting in low Pb availability. Jurinak and Santillan Medrano (1974) attributed the high Pb retention to hydroxides and hydroxy phosphate in acid soils, and to carbonates in calcareous soils.

Increasing the soil pH, as well as the CEC and P levels, resulted in a decrease in soil Pb availability. Large application of Pb to a soil having a pH level of 5.0 does not result in yield reduction or accumulation of lead in plant tissue. The highest level of Pb is found in plant roots, and its value in other plant parts diminishes in the order: shoot, fruit and seeds. Its typical concentration in crop tissue is 0.1-10 mg/kg (Page et al. 1981).

High doses of Pb from $Pb(NO_3)_2$ and petrol greatly decrease the yield and uptake of nutrients. This may be due to the formation of insoluble compounds of Pb such as basic lead phosphate resulting in the collapse of the plant tissue and altered growth.

Misra and Kumar (1991) used Pb and Ca as nutrients for biomass yield of turnip. They found the highest yield in the combination Pb 50% and Ca 20%. The presence of 50 and 100 mg Pb/kg in soil alongwith 2% Ca gave bettter yield than 1% Ca. The yield of turnip was affected to maximum at Pb 200 mg/kg with 1% and 2% Ca.

The typical range of Zn in plant tissues is 15-200 mg/kg. Zinc is toxic to plants at different

concentrations, typical value being 200 mg/kg. The level in forage foliage is 500-1500 mg/kg. Zinc toxicity is a greater problem for plants than for animals or humans.

The prevalant zinc form in the solution of acid soils in Zn^{2+}, this is the Zn form taken up by plants. The main factors responsible for Zn retention in soils are sorption by clay, hydrous oxide surface reactions, and chelation by organic matter. The Zinc availability is reduced by phosphate and liming more than that of Cd, Cu and Ni.

High amount of available Zn in soils may lead to high figures for Zn in plants; much more in the vegetable parts than in seeds. In an experiment representative of the 1970s Boawn (1971) reports several leafy vegetable crops grown in the field accumulating 300 or even 400 ppm without damage. When Zn was added upto 0.9 mg/100 g of a soil of pH. 6.1, of the 12 crops grown, only swiss chard and spinach were damaged at this high rate, and swiss chard in particular was collector, ranging to cover 800 ppm Zn.

Copper is required by plants but is also considered as one of the elements of a potentially

serious hazard, when present in excessive level as in the case of certain sewage sludge soils. Cu toxic level in plants is >25 mg/kg dry matter. Severe Cu toxicity may occur when there is excess Cu accumulation in the roots, but translocation to the top parts of plants is limited. The toxicity of Cu is greater than that of Zn.

The Cu content of normal plants, even with high application of Cu, rarely exceeds 30 ppm unless damage has been done. Thus it acumulates less easily in plants growing on metalliferous soil than Zn and Ni. The Cu in seed does not increase with addition to the soil.

Dev and Mann (1972) reported that increasing level of P application significantly decreased the available Fe, in sandy loam soil. Pathak et al. (1972) observed a positive and significant relationship between avaibale P and Mn concentration at different fertility level. Hulagur et al. (1975) observed reduced concentration and uptake of Cu by P application.

Ryden and Pratt (1980) reported that excessive level of available P may result in nutrients imbalances, such as Cu, Fe and Zn deficiencies.

Misra and Tiwari (1987) observed the effect of Mussoorie rock phosphate on the uptake of heavy metals and reported that addition of MRP reduces the uptake of heavy metals in fenugreek with sewage sludge treated soil.

Wallace and Cha (1989) observed that the Bush bean plants grown in nutrient solution resulted in stresses of $CaCO_3$ (Cu deficiency) excess Cu, and P deficiency. When moderate P deficiency and high Cu toxicity were both simultaneously imposed, the interaction resulting in poor growth was synergistic when the solution pH was about 4. When the solution pH was about 8 the interaction was less synergistic. The high pH considerably suppressed the uptake of Cu. The results are further an evidence that liming can decrease much of the interactive synergistic effects of toxic concentrations of multiple trace metals. Low P resulted in increased Cu in roots at the low pH. The P deficiency was more conducive to Fe deficiency induced by high Cu than was adequate P.

Misra and Kumar (1994) observed that phosphate from Mussoorie rock phosphate becomes available and forms complexes with the added heavy metals thereby

decreasing the availability of heavy metals, especially Fe and Cr to fenugreek.

EXPERIMENTAL DETAILS:

(I) Experiment with Fenugreek:

The experiment was conducted at Sheila Dhar Institute experimental farm in order to findout the effect of different doses of Mussoorie rock phosphate (viz 100, 200, 300, 500, 700 kg/ha) and sewage irrigation on the growth, yield and uptake of heavy metals viz Cu, Cr, Pb, Zn and Fe.

The crop was sown on 20 October 1992 at the rate of 30 kg/ha. The crop was irrigated with domestic sewage water. MRP was applied 20 days before sowing in the microplots, ($1m^2$). The number of total treated plots was 18.

Treatments:

1.	T_0 S	MRP 0 + Sewage
2.	T_1 S	MRP 100 kg/ha + Sewage
3.	T_2 S	MRP 200 kg/ha + Sewage
4.	T_3 S	MRP 300 kg/ha + Sewage
5.	T_4 S	MRP 500 kg/ha + Sewage
6.	T_5 S	MRP 700 kg/ha + Sewage

The crop was uprooted after 60 days of sowing.

Total heavy metals (viz. Cu, Cr, Pb, Zn, Fe) present in dried biomass were detected directly in tri-acid mixture extract using Atomic Absorption Spectrophotometer.

The results are given in Tables 5.1 and 5.2.

Results:

The uptake of heavy metals by fenugreek decreases gradually with increasing doses of MRP. The uptake of Fe is greater and Cr uptake is lower than other heavy metals. But the uptake of Pb is suddenly decreased.

It is noteworthy that the concentration of heavy metals in MRP treated plots decreased. However, the reduction in Fe and Pb is greater than in other heavy metals.

As the uptake of the heavy metals depends on the availability of heavy meatals in soil, so when trend of uptake is compared with the available heavy metals, it is clear that uptake of heavy metals reduced with decreased availability.

It is also noticeable that this uptake is not governed by a similar trend but is different

heavy metals and crops and other stresses.

The ratio between available heavy metals in soil and uptake by fenugreek is about 40 to 50

In case of Cr the relationship between available Cr in soil and its uptake is highly correlative, the Cr uptake is 84% in T_0S and 65% in T_5S. Uptake of Pb is also similar to Cr.

Table 5.1 : Uptake of heavy metals by fenugreek leaves.

Treatment	Heavy metals (ppm)				
	Zn	Cr	Cu	Pb	Fe
T_0 S (Control only sewage)	4.9	2.7	3.8	3.4	10.3
T_1 S (100 kg/ha MRP + Sewage)	3.2	2.2	3.4	3.0	8.8
T_2 S (200 kg/ha MRP + Sewage)	3.0	2.0	3.2	2.2	7.1
T_3 S (300 kg/ha MRP + Sewage)	2.8	1.9	2.9	2.0	6.8
T_4 S (500 kg/ha MRP + Sewage)	2.6	1.6	2.0	1.9	6.2
T_5 S (700 kg/ha MRP + Sewage)	2.0	1.3	1.7	1.4	5.9
	r =0.73	r=0.78	r=0.83	r=0.89	r=0.92

Table 5.2 : Available concentration of heavy metals in soil.

Treatments	Heavy metals (ppm)				
	Zn	Cr	Cu	Pb	Fe
T_0 S (Control, only Sewage)	9.9	3.2	6.2	6.0	23.0
T_1 S (100 kg/ha MRP + Sewage)	7.8	2.9	5.1	4.8	19.0
T_2 S (200 kg/ha MRP + Sewage)	6.3	2.8	4.9	3.9	18.2
T_3 S (300 kg/ha MRP + Sewage)	5.2	2.6	4.7	3.6	16.2
T_4 S (500 kg/ha MRP + Sewage)	4.7	2.4	4.2	3.0	12.3
T_5 S (700 kg/ha MRP + Sewage)	4.1	2.0	4.0	2.7	11.8
r=	0.72	r=0.79	r=0.81	r=0.83	r=0.90

(II) <u>Experiment with Spinach</u>:

The field experiment was conducted at the same plot in order to findout the residual effect of MRP on the growth , yield and uptake of heavy metals viz, Cu, Cr, Pb, Zn and Fe.

Spinach was sown as a test crop. The sowing was done on 10th January 1993 at the rate of 20 kg/ha.

The crop was irrigated with sewage water.

Treatments :

1. R_0 S — MRP 0+Sewage
2. R_1 S — MRP 100 kg/ha + Sewage
3. R_2 S — MRP 200 kg/ha + Sewage
4. R_3 S — MRP 300 kg/ha + Sewage
5. R_4 S — MRP 500 kg/ha + Sewage
6. R_5 S — MRP 700 kg/ha + Sewage

Crop was uprooted after 60 days of sowing. The total heavy metals (viz, Cu, Cr, Pb, Zn and Fe) present in dried biomass were detected directly in tri-acid mixture extract using Atomic Absorption Spectrophotometer. The resutls are reported in Tables 5.3 and 5.4.

Table 5.3 : Uptake of heavy metals by spinach leaves.

Treatments	Heavy metals (in ppm)				
	Zn	Cr	Cu	Pb	Fe
R_0 S (Control, only Sewage)	6.1	2.9	4.0	3.8	14.9
R_1 S(100 kg/ha MRP +Sewage)	3.0	2.1	3.2	2.9	8.01
R_2 S(200 kg/ha MRP + Sewage)	2.8	1.8	3.0	2.0	7.00
R_3 S(300 kg/ha MRP + Sewage)	2.5	1.5	2.6	1.9	6.30
R_4 S(500 kg/ha MRP + Sewage)	2.1	1.2	1.6	1.5	6.00
R_5 S(700 kg/ha MRP + Sewage)	1.8	1.0	1.2	1.1	5.20
	r =0.78	r=0.81	r=0.87	r=0.88	r=0.91

Table 5.4 : Available concentration of heavy metals in soil.

Treatments	Heavy metals (in ppm)				
	Zn	Cr	Cu	Pb	Fe
R_0 S (Control, only Sewage)	14.9	3.9	6.9	6.8	29.0
R_1 S (100 kg/ha MRP + Sewage)	7.6	2.9	5.0	4.5	18.2
R_2 S (200 kg/ha MRP + Sewage)	6.1	2.6	4.6	3.6	17.0
R_3 S (300 kg/ha MRP + Sewage)	5.0	2.3	4.2	3.2	14.7
R_4 S (500 kg/ha MRP + Sewage)	4.0	2.0	4.0	2.8	11.2
R_5 S (700 kg/ha MRP + Sewage)	3.9	1.9	3.6	2.0	10.2
	r=0.78	r=0.81	r=0.87	r=0.88	r=0.91

Results:

The available P_2O_5 (kg/ha) in various treatments shows that it follows increasing doses of MRP added previously.

The uptake of heavy metals by spinach reduced as available P_2O_5 of the soil increased. The uptake of all the heavy metals decreased as available P_2O_5 increased. This shows that phosphate has got

antagonistic effect on the uptake of heavy metals.

The concentration of available Fe, Cu, Pb and Cr decreased as the available phosphate increased. It shows that Zn x P interaction leads to soluble compound of Zn with P. Thus MRP is able to antagonise the availablity of heavy metals even in the second crop.

The concentration of heavy metals is higher in control plots because only sewage water was used for irrigation. Similarly concentration of heavy metals in control plot is higher than in experiment I, in control plot. Its main cause is repeated use of sewage irrigation.

(III) Experiment with Fenugreek:

The experiment was conducted at Sheila Dhar Institute experimental farm in order to find out the effect of different doses (i.e. @ 100, 200, 300, 500, 700 kg/ha) of Mussoorie Rock phosphate (MRP) on the growth, yield and uptake of heavy metals viz. Cu,Cr,Pb, Zn and Fe by fenugreek which had been grown previously also.

The two factors (sewage and MRP) were combined into six treatments and replicated thrice. MRP doses were applied 20 days before sowing. Fenugreek was sown

on 15 October 1993. The crop was irrigated by sewage water.

Treatments :

1.	P_0 S	MRP 0 + Sewage
2.	P_1 S	MRP 100 kg/ha + Sewage
3.	P_2 S	MRP 200 kg/ha + Sewage
4.	P_3 S	MRP 300 kg/ha + Sewage
5.	P_4 S	MRP 500 kg/ha + Sewage
6.	P_5 S	MRP 700 kg/ha + Sewage

The test crop was uprooted after 60 days of sowing.

The total heavy metals (i.e. Cu, Cr, Pb, Zn and Fe) present in dried biomass were detected directly in tri-acid mixture extract using Atomic Absorption Spectrophotometer.

The results are given in Tables 5.5 and 5.6.

Table 5.5: Uptake of heavy metals by fenugreek leaves.

Treatments	Heavy metals (in ppm)				
	Zn	Cr	Cu	Pb	Fe
P_0 S (Control, only Sewage	7.1	3.2	4.7	3.9	16.4
P_1 S (100 kg/ha MRP + Sewage)	2.9	2.0	3.1	2.6	7.3
P_2 S (200 kg/ha MRP + Sewage)	2.6	1.6	2.8	1.7	6.1
P_3 S(300 kg/ha MRP + Sewage)	2.3	1.3	2.4	1.5	6.0
P_4 S(500 kg/ha MRP + Sewage)	1.9	1.0	1.3	1.1	5.9
P_5 S(700 kg/ha MRP + Sewage)	1.1	0.7	0.9	0.8	5.0
	r=0.78	r=0.79	r=0.84	r=0.89	r=0.92

Table 5.6: Available concentration of heavy metals in soil.

Treatments	Heavy metals (in ppm)				
	Zn	Cr	Cu	Pb	Fe
P_0 S (Control, only Sewage)	16.7	4.3	7.2	7.0	33.1
P_1 S (100 kg/ha MRP + Sewage)	7.2	2.6	4.1	4.1	17.8
P_2 S (200 kg/ha MRP + Sewage)	6.0	2.4	4.0	3.2	16.2
P_3 S (300 kg/ha MRP + Sewage)	4.8	2.1	3.6	3.0	14.3
P_4 S (500 kg/ha MRP + Sewage)	3.8	1.7	3.2	2.4	11.0
P_5 S (700 kg/ha MRP + Sewage)	3.7	1.2	3.0	1.8	10.0
	r=0.78	r=0.81	r=0.87	r=0.89	r=0.93

Results:

In experiment III, the different doses of MRP were added in the same plots. The uptake of heavy metals by fenugreek leaves was near similar to MRP doses. However, the concentration of heavy metals in leaves is higher than in experiment I.

The uptake of Fe is greater than other heavy metals, and even the content of Fe in control plot is higher than in experiment I. But decrease in the Fe content follows increasing doses of MRP.

The uptake of other heavy metals is similar to experiment I and the decreases also follows increasing doses of MRP.

The availability of heavy metals reduced alongwith increasing doses of MRP. In case of Zn, the availability is much lower than in experiment II. The rest heavy metals decreased with increasing doses of MRP.

(IV) **Experiment with Radish:**

Field experiment was conducted at Sheila Dhar Institute experimental farm, in order to findout the effect of different doses of MRP (@ 100, 200, 300, 500, 700 kg/ha) on growth, biomass and uptake of heavy

metals (viz. Cu, Cr, Pb, Zn and Fe) by radish in sewage irrigated soil. MRP was applied 20 days before sowing the test crop.

<u>**Treatments**</u> :

1.	T_0	MRP 0 + Sewage
2.	T_1	MRP 100 kg/ha + Sewage
3.	T_2	MRP 200 kg/ha + Sewage
4.	T_3	MRP 300 kg/ha + Sewage
5.	T_4	MRP 500 kg/ha + Sewage
6.	T_5	MRP 700 kg/ha + Sewage

The sowing was done on 15 January 1994, in randomized blocks at the rate of 12 kg/ha. The test crop was irrigated with sewage water, and it was uprooted after 60 days of sowing. The total biomass was recorded separately for roots and shoots.

The heavy metals were determined separately in the roots and shoots.

The total heavy metals (i.e. Cu, Cr, Pb, Zn and Fe) present in dried biomass were detected in triacid mixture extract , using Atomic Absorption Spectrophotometer.

The results are given in Tables 5.7, 5.8 and 5.9.

Table 5.7 : Uptake of heavy metals by radish leaves.

Treatments	Heavy metals (in ppm)				
	Zn	Cr	Cu	Pb	Fe
T_0 (Control, only Sewage)	7.4	3.6	4.8	4.1	19.0
T_1 (100 kg/ha MRP + Sewage)	1.6	1.5	2.7	1.9	7.1
T_2 (200 kg/ha MRP + Sewage)	1.2	1.0	1.7	1.1	5.7
T_3 (300 kg/ha MRP + Sewage)	0.9	0.7	1.3	0.9	5.1
T_4 (500 kg/ha MRP + Sewage)	0.7	0.4	0.9	0.6	4.8
T_5 (700 kg/ha MRP + Sewage)	0.4	N.A.	0.6	0.4	4.2
	r=0.79	r=0.83	r=0.87	r=0.89	r=0.92

Table 5.8 : Uptake of heavy metals by radish roots.

Treatments	Heavy metals (in ppm)				
	Zn	Cr	Cu	Pb	Fe
T_0 (Control, only Sewage)	1.7	0.9	1.0	0.9	7.6
T_1 (100 kg/ha MRP + Sewage)	0.7	0.4	0.9	0.5	2.3
T_2 (200 kg/ha MRP + Sewage)	0.5	0.3	0.9	0.3	2.0
T_3 (300 kg/ha MRP + Sewage)	0.4	0.2	0.7	0.2	1.7
T_4 (500 kg/ha MRP + Sewage)	0.3	0.1	0.5	0.1	1.2
T_5 (700 kg/ha MRP + Sewage)	0.2	N.A.	0.3	0.1	1.0
	r=0.80	r=0.82	r=0.88	r=0.89	r=0.93

Table 5.9 : Available concentration of heavy metals in soil.

Treatments	Heavy metals (in ppm)				
	Zn	Cr	Cu	Pb	Fe
T_0 (Control, only Sewage)	16.4	4.8	7.7	7.2	37.4
T_1 (100 kg/ha MRP + Sewage)	6.3	1.9	4.0	2.5	17.2
T_2 (200 kg/ha MRP + Sewage)	5.0	1.8	3.9	2.0	16.0
T_3 (300 kg/ha MRP + Sewage)	4.6	1.7	3.2	1.9	14.0
T_4 (500 kg/ha MRP + Sewage)	3.2	1.5	3.0	1.6	10.4
T_5 (700 kg/ha MRP + Sewage)	3.0	1.3	2.7	1.4	9.1
	r=0.81	r=0.87	r=0.88	r=0.91	r=0.96

General Discussion:

It is clear from the data regarding growth and yield of four crops (viz. Fenugreek, Spinach, Fenugreek and Radish) that there is no harmful effect of sewage on their vegetative growth but there is definite increase in the content of heavy metals in these crops when only sewage water is used continuously for irrigation.

However, when Mussoorie rock phosphate (MRP) was

added in combination with sewage water, the concentration of heavy metals like Zn, Cr, Pb, Fe was reduced with increasing doses of MRP. The content of Fe alone showed higher level in vegetative portion of plants.

The decrease in the content of heavy metals viz. Cr and Pb after the addition of MRP can be ascribed to antagonistic effect of phosphate on the availability of these heavy metals. Though Fe X P interaction can immobilize Fe, yet increased uptake can be explained due to higher amount of Fe in the sewage water. Fe is normaly the most abundant heavy metal in leafy vegetable crops and in sewage sludge of both domestic and industrial origin.

The Zn content is lower than Fe content in plant material. The Zn uptake increased due to higher content of Zn in the sewage.

The Cu content reduced alongwith increasing doses of MRP, but the concentration of Cu increased in control plot. This may be due to presence of Cu in sewage water.

The Pb content in plant material reduced alongwith increasing doses of MRP. The content of Pb

increased in order of increasing sewage application, but the uptake reduced with increasing doses of MRP.

The Cr content is lowest as compared to other heavy metals and uptake by plant was decreased alongwith increasing doses of MRP.

The content of heavy metals uptake by crops can be written in the following order.

Fe > Zn > Cu > Pb > Cr.

Perhaps excessive level of available phosphate results in the formation of complexes of Cu, Fe and Zn, so that the availability of these metals is reduced for different crops.

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CHAPTER VI

CHAPTER - VI

INTERACTION OF HEAVY METALS:

Olsen (1972) defined interaction as: (i) an influence, a mutual or reciprocal action of one element upon another in relation to plant growth and (ii) differential response to one element in combination with varying levels of a second element applied simultaneously. Conceptualising the physical mode in interaction in crop production, Rusell (1973) states: If two factors are limiting or nearly limiting growth, addition of only one of them will have little effect on growth, whilst adding both together will have a very considerable effect. Two such factors are said to have a positive interaction in such circumstances, for the response of the crop to both together is larger than the sum of the response to each separately. If the crop response to the two factors together equalled the sum of its responses to each separately, we would say that the two factors showed no effect and they worked entirely independently of each other, and if the response to the two factors together was less than the sum of the responses to each factor separately, they are said to have negative interaction with each other.

It can be generalised that when factors in

combination result in growth response that is greater than the sum of their individual effects, the interaction is positive and when the combined effects are less, the interaction is negative. Thus, depending upon the combined effects, the interactions could be synergistic (positive), antagonistic (negative) or simply additive, the last one would mean non existence of any interaction. In literature on interactions, the highest dry matter yields, nutrient content and uptake obtained with a combination of factors have often been described synergistic. However under the framework of Russell (1973), there could be the cases of either synergism or antagonism or simple additivite.

INTERACTION WITH PHOSPHATE:

The interactions between heavy metals and phosphate deserve some comment because of the high content of P in sewage sludges and the widespread use of phosphatic fertilizers. Among the metals, Zn has received most attention, especially in the USA where additions of phosphatic fertilizers have caused Zn deficiency in many crops.

There in evidence that this is not a soil effect (Olsen, 1972) and that phosphate reduces transport of

Zn in the plant, most likely that from roots to shoots. The interaction with phosphate raises the possibility that plants may be protected against injury from some heavy metals when the phosphate supply is high.

Phosphate induced zinc deficiency has been the topic of intensive investigation and reviews (Randhawa et al. 1979, Katyal et al. 1992, Tondon 1992). The possible causes identified by Olsen (1972) of Zn-P interaction include:

(i) interaction in soil

(ii) slower rate of transloction of Zn from the roots to the tops.

(iii) simple dilution effect on Zn concentration in the tops owing to the growth response of P .

(iv) metabolic disorder within plant cells related to an imbalance between P and Zn.

Takkar et al. (1976) reported that the optimum grain yield of maize ocurred at 44 kg P/ha and the high P supply beyond this optimum produced severe deficiency symptoms in no zinc treatment and resulted in significant decrease in grain yield on P and Zn deficient Fatehpur loamy sand.

Takkar et al. (1976) concluded that at low tissue P-Zn ratios obtained at low soil P-level, yields were

low, consistent with the P deficiency symptoms and at higher P-Zn ratios obtained with high soil P and zero Zn application, severe Zn deficiency symptoms were observed and the yield reduced drastically.

Higher doses of phosphatic fertilizers have been implicated with reduction in both zinc content and its uptake by the crop plants (Safaya 1976, Singh and Singh 1979, Bhogal et al. 1985 and Takkar et. al 1989).

Numerous reports of induced Zn deficiency in crops with application of P have been recorded at many places in India. P-Zn interaction occurred in soil because added P was found to decrease the available Zn content and less soluble P carriers did not affect the extractable Zn.

Sanyal and Deb (1976) remarked that zinc application showed beneficial effect on applied P recovery as well as on $NaHCO_3$. extractable P in soil irrespective of reaction period due to the fact that $Zn_3(PO_4)_2 \cdot 4H_2O$ was fairly soluble in soil.

Application of P has been shown to result in the formation of different reaction products of colloidal and amorphous Fe-Al phosphate in different soils and caused a decrease in its translocation to shoot. Some

workers noticed that high Fe (beyond 10 ppm added as Fe-EDTA) decreased yield and uptake of P by sorghum. The magnitude of this effect was more at low than at high P rates of application.

Interactive effects of iron and phosphates are generally antagonistic (Dangarwala 1992) with depressive effects of excessive Fe on P utilisation being attributed to the precipitation of $Fe_3 (PO_4)_2$ on the root sufaces (Chahal et al. 1979). In vertisols of Coimbatore, increasing level of Fe and P reduced each other's availability (Takkar et al. 1989).

Bhumbla et al. (1969) reported that ferrous iron content of soil increased with decreasing pH.

Gupta et al. (1983) reported that uptake of iron was reduced considerably with an increase in added phosphorus.

Chattarjee et al. (1983) informed the effect of P on the availability of Fe. A laboratory incubation study was carried out to study the effect of application of different levels of P and Zn on the changes in the content of extractable Fe in a waterlogged soil. DTPA Fe recorded an increase upto 15 days of incubation and thereafter it declined. The

initial rise in the content might be attributed to reduction of higher oxides of Fe to soluble ferrous compounds by anaerobic micro-organisms during their respiration. The decline observed might be due to decrease in dissolved CO_2 concentration resulting in a condition favourable for the hydrolysis of Fe^{++} and its subsequent oxidation to Fe $(OH)_3$.

Dev and Mann (1972) reported that increasing level of P application significantly decreased the available Fe in sandy loam soil.

Relationship between the decrease in available P has been associated with the increase in available Fe and with the increase in the adsorption/reduction of Cr (VI) by the soil.

The effect of different ions (Fe and P) on the nutrient solution containing Cr (VI) on the uptake and translocation of Cr by wheat plant was studied by Cary et al. (1977). The removal of Cr (VI) from the nutrient solution was very much reduced in the absence of Fe. However, the translocation of Cr was greater to the tops from nutrient solution deficient in Fe. The translocation of Cr was also substantially greater in plants grown in P-deficient nutrient solution even

though Cr removal from nutrient solution slightly depressed.

Barlett and Kimble (1976) studied the relative adsorption of Cr (VI) and P in 24 hours from aqueous medium containing Cr (VI) and P as $KH_2 PO_4$. In soil with low organic matter having high capacity to adsorb phosphate, they found that Cr (VI) was not adsorbed by the soil in the presence of excess orthophosphates in the medium. The investigators concluded that Cr (VI) and phosphate competed for the same adsorption sites. Even though chromate is tightly bound by the soils. yet it is replaceable by phosphate. In contrast, the phosphate could not prevent the decrease in equilibrium concentration of Cr (VI) in soil containing high level of organic matter. The decrease in Cr(VI) concentration was either due to reduction of Cr (VI) by organic matter or else adsorbed Cr (VI) was not replaceable by phosphate.

Cary et al. (1977) studied Fe and Cr concentration in different parts of different plants grown in adjacent fields. The results indicated a positive relationship between Fe and Cr concentration. In the range of about 0.02 ppm to 0.60 ppm Cr in the plant parts, the Fe concentration varied from about 20

ppm to 400 ppm. This evidence suggests that the plants which accumulate Fe will also accumulate Cr.

Bingham (1958) reported a Cu-P interactions and observed that application of P to soils depressed Cu concentration in plants. Similar reports have been made by a large number of workers with field crops and tree species. The concentration of Cu in sour orange seedlings decreased on increasing the levels of P in rainfed sand (Bingham 1963).

According to Halagur et al. (1975) there is a reduced concentration and uptake of Cu by P application. However Sadaphal and Das (1963) and Dakhor et al. (1963) obtained a positive interaction between Cu and P in the case of wheat crop.

On a loamy sand soil of Haryana, deficient in both available Cu (DTPA Cu, 0.31 ppm) and P (Olsen P 4.2 ppm) application of 50 ppm Cu adversely affected yield and P concentration in wheat and 250 ppm significantly reduced the yield and Cu content (Singh and Singh 1979). Application of the affected nutrient counteracted the adverse effect of the other.

However, in wheat and sorghum grown in medium

black soil, P application did not markedly affect the Cu concentration of the plants (Badhe and Mundwaik 1982). In rainfed wheat grown under field conditions, the grain and straw yield were increased as also N and K uptake when Cu was applied but it significantly depressed P uptake and concentration in straw (Venkateswarlu and Misra 1987). Similarly, Cu application to rice increased the dry matter, total leaf chlorophyll but decreased P concentration in the plant (Eun, 1981). On application of phosphatic fertilizers in flooded rice fields, the decrease in Cu concentration in plants might be due to the formation of copper phosphate, which is not readily available to plants. An antagonistic effect of Cu and P in rice was observed when one of the nutrients was applied in large quantity (Alam 1983).

Lead is strongly precipitated by soil yet many plants take up as much as 30 ppm in their roots. Most plants retain this Pb almost entirely in the roots while it may generally be right to ignore Pb in roots since it does not move into the tops. Such movement was noted for sulphur deficient ryegrass, which accumulated over 25 ppm in tops (Jones et al. 1973).

Increasing doses of phosphate lead to decrease the availability of Pb due to formation of precipitate of phosphate and which contributes towards the insolubility of Pb (Machlean 1969, Dedolph et al. 1970, Miller and Koeppe, 1970, Cox and Rains, 1972).

Increasing doses of phosphate along with Pb lead to a decrease in the amount of avilable Pb which has tendency to decrease further with time. The amount of available P decreased with time when Pb is being added. (Misra and Pandey 1975).

EXPERIMENTAL DETAILS:

The location of the experiment was the same (Sheila Dhar Institute experimental farm) as in the uptake experiments, surface soil samples of the field plots to be used were analysed in detail for any deviation in their metal contents (Tables 6.1 to 6.5).

Table 6.1 : Interaction between Zinc and Phosphorus.

(in ppm)

Treatments	Experiment I	Experiment II	Experiment III	Experiment IV
	Available Zn	Available Zn	Available Zn	Available Zn
Control (Only Sewage irrigated soil)	9.9	14.9	16.7	16.4
100 kg/ha MRP + Sewage irrigated soil	7.8	7.6	7.2	6.3
200 kg/ha MRP + Sewage irrigated soil	6.3	6.1	6.0	5.0
300 kg/ha MRP + Sewage irrigated soil	5.2	5.0	4.8	4.6
500 kg/ha MRP + Sewage irrigated soil	4.7	4.0	3.8	3.2
700 kg/ha MRP + Sewage irrigated soil	4.1	3.9	3.7	3.6
	r=0.73	r=0.75	r=0.77	r=0.86

In table 6.1 data are presented regarding interaction between added phosphate and zinc available through sewage irrigation. It is observed that available Zn content of soil gradually decreased with increasing doses of added MRP. The four controls clearly indicate that avaibale Zn in soil increased due

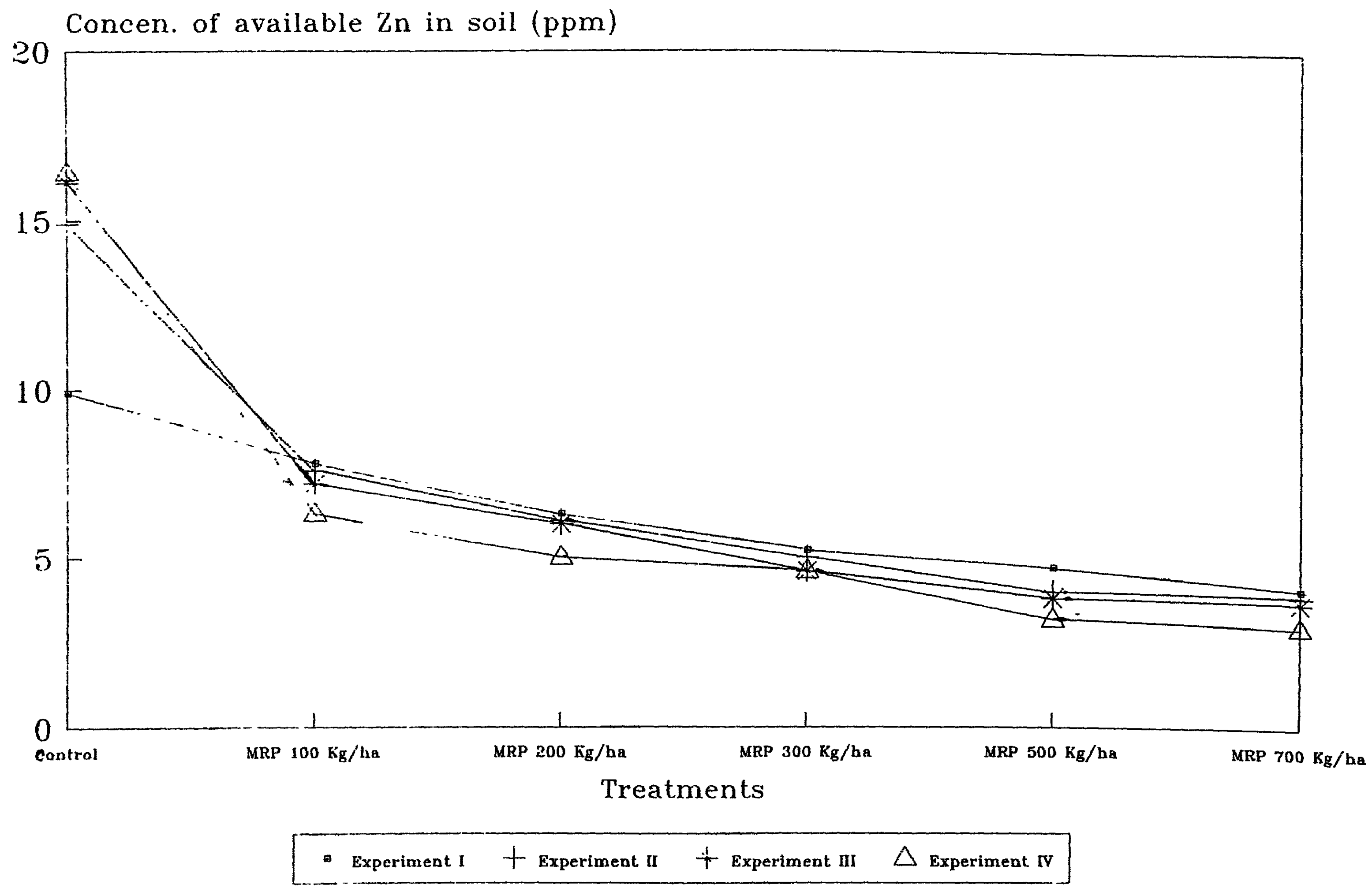

Fig. 6.1 Interaction between Zn and P in soil

to repeated irrigation of the crops with sewage. However available Zn in soil decreased due to the MRP addition. This decrease definitely points to an interaction between available Zn of the soil and P that is made soluble from MRP due to sewage irrigation. It is also clear that only a part of solubilized P from MRP would have reacted with Zn to form zinc phosphate which is partly soluble and hence available to the crops.

Table 6.2 : Interaction between Chromium and Phosphorus (in ppm)

Treatments	Experiment I	Experiment II	Experiment III	Experiment IV
	Available Cr	Available Cr	Available Cr	Available Cr
Control (Only Sewage irrigated soil	3.2	3.9	4.3	4.8
100 kg/ha MRP + Sewage irrigated soil	2.9	2.9	2.6	1.9
200 kg/ha MRP + Sewage irrigated soil	2.8	2.6	2.4	1.8
300 kg/ha MRP + Sewage irrigated soil	2.6	2.3	2.1	1.7
500 kg/ha MRP + Sewage irrigated soil	2.4	2.0	1.7	1.5
700 kg/ha MRP + Sewage irrigated soil	2.0	1.9	1.2	1.3
	r=0.79	r=0.81	r=0.83	r=0.85

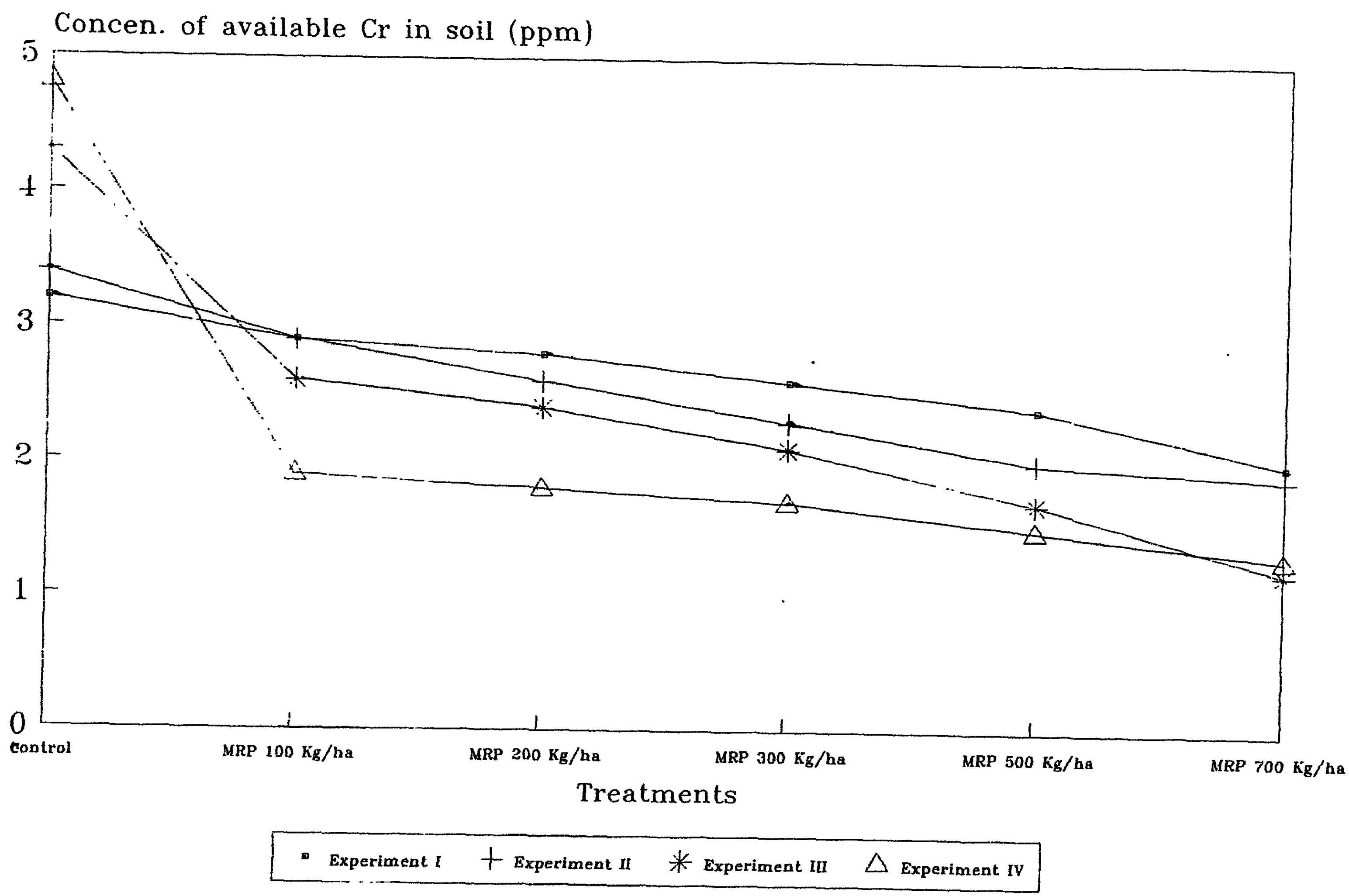

Fig. 6.2 Interaction between Cr and P in soil

Table 6.2 presents the interactions between chromium and phosphate. Available Cr in controls shows an increasing trend because of the addition of Cr through sewage irrigation. However, inclusion of MRP in different doses to the soil resulted in decreased avaialble Zn of the soil. The greater dose of MRP, the smaller is the available Cr in soil. Also, the last crop (radish) appears to have reduced available Cr.

Table 6.3 : Interaction of Copper and Phosphorus

(in ppm)

Treatments	Experiment I	Experiment II	Experiment III	Experiment IV
	Available Cu	Available Cu	Available Cu	Available Cu
Control (Only Sewage irrigated soil	6.2	6.9	7.2	7.7
100 kg/ha MRP + Sewage irrigated soil	5.1	5.0	4.1	4.0
200 kg/ha MRP + Sewage irrigated soil	4.9	4.6	4.0	3.9
300 kg/ha MRP + Sewage irrigated soil	4.7	4.2	3.6	3.2
500 kg/ha MRP + Sewage irrigated soil	4.2	4.0	3.2	3.0
700 kg/ha MRP + Sewage irrigated soil	4.0	3.6	3.0	2.7
	r=0.80	r=0.83	r=0.84	r=0.89

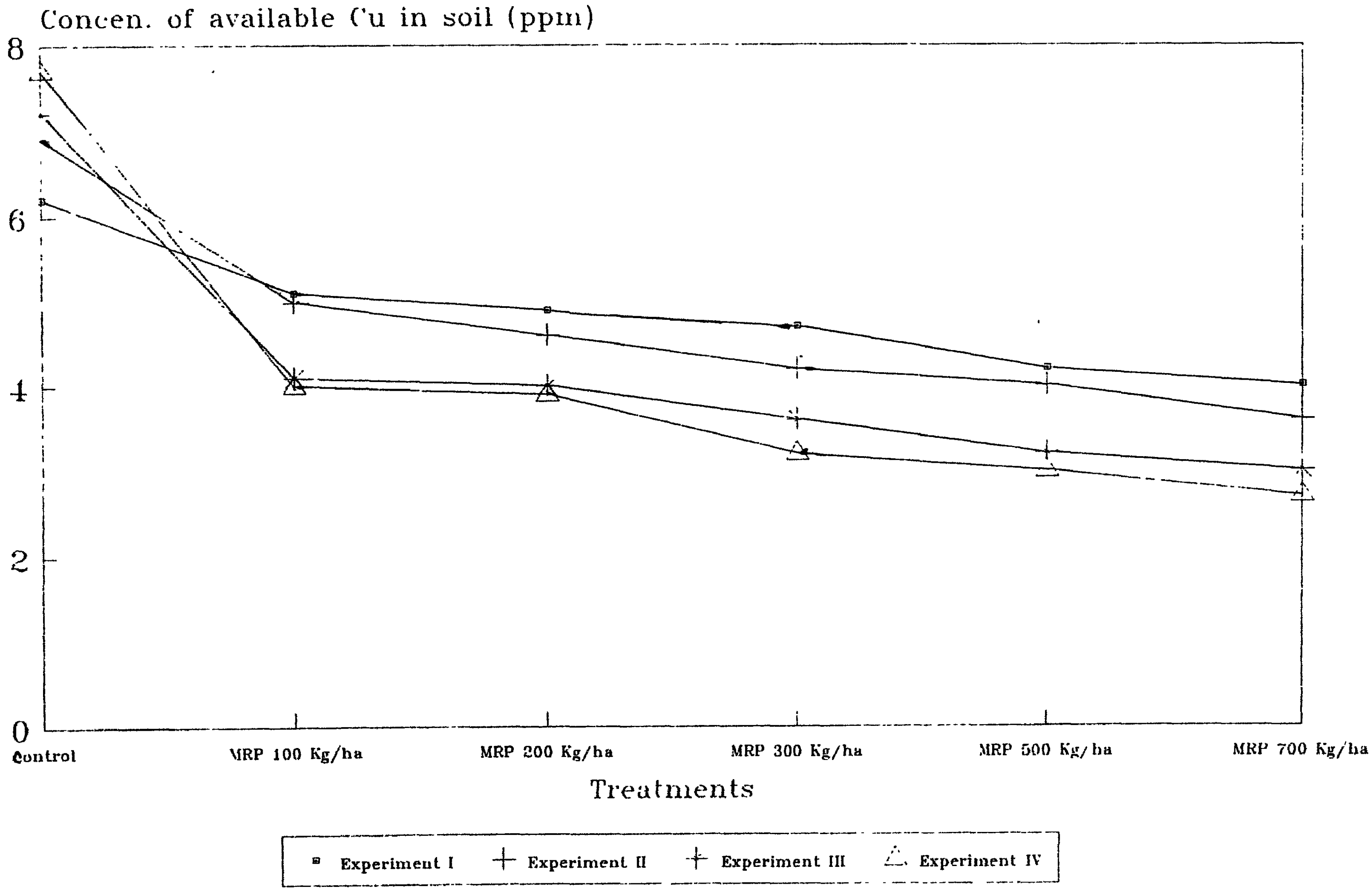

Fig. 6.3 Interaction of Cu and P in soil

Interaction of copper and phosphorus is presented in the table 6.3. In comparison to controls, the available Cu in soil has decreased in proportion to the additions of MRP. Highest dose of MRP showed maximum effect in decreasing available Cu in the soil. Similarly of the various crops, radish decreased available Cu to the maximum. This may be crop effect as well as the increasing solubility of MRP with time.

While, Cu X P interaction is mostly significant, but may be that available Cu decreases due to the formation of copper phosphate in soil.

Table 6.4 presents the interaction between lead and phosphate in soil. Although Pb in soil is highest in the control plot of experiment IV, but there is a sharp decrease in available Pb of the soil with doses of MRP.

Available Pb in the MRP treated soil shows a similar trend as Zn and Cu.

Table 6.4 : Interaction of Lead and Phosphorus

(in ppm)

Treatments	Experiment I Available Pb	Experiment II Available Pb	Experiment III Available Pb	Experiment IV Available Pb
Control (Only Sewage irrigated soil)	6.0	6.8	7.0	7.2
100 kg/ha MRP + Sewage irrigated soil	4.8	4.5	4.1	2.5
200 kg/ha MRP + Sewage irrigated soil	3.9	3.6	3.2	2.0
300 kg/ha MRP + Sewage irrigated soil	3.6	3.2	3.0	1.9
500 kg/ha MRP + Sewage irrigated soil	3.0	2.8	2.4	1.6
700 kg/ha MRP + Sewage irrigated soil	2.7	2.0	1.8	1.4
	r=0.74	r=0.76	r=0.79	r=0.86

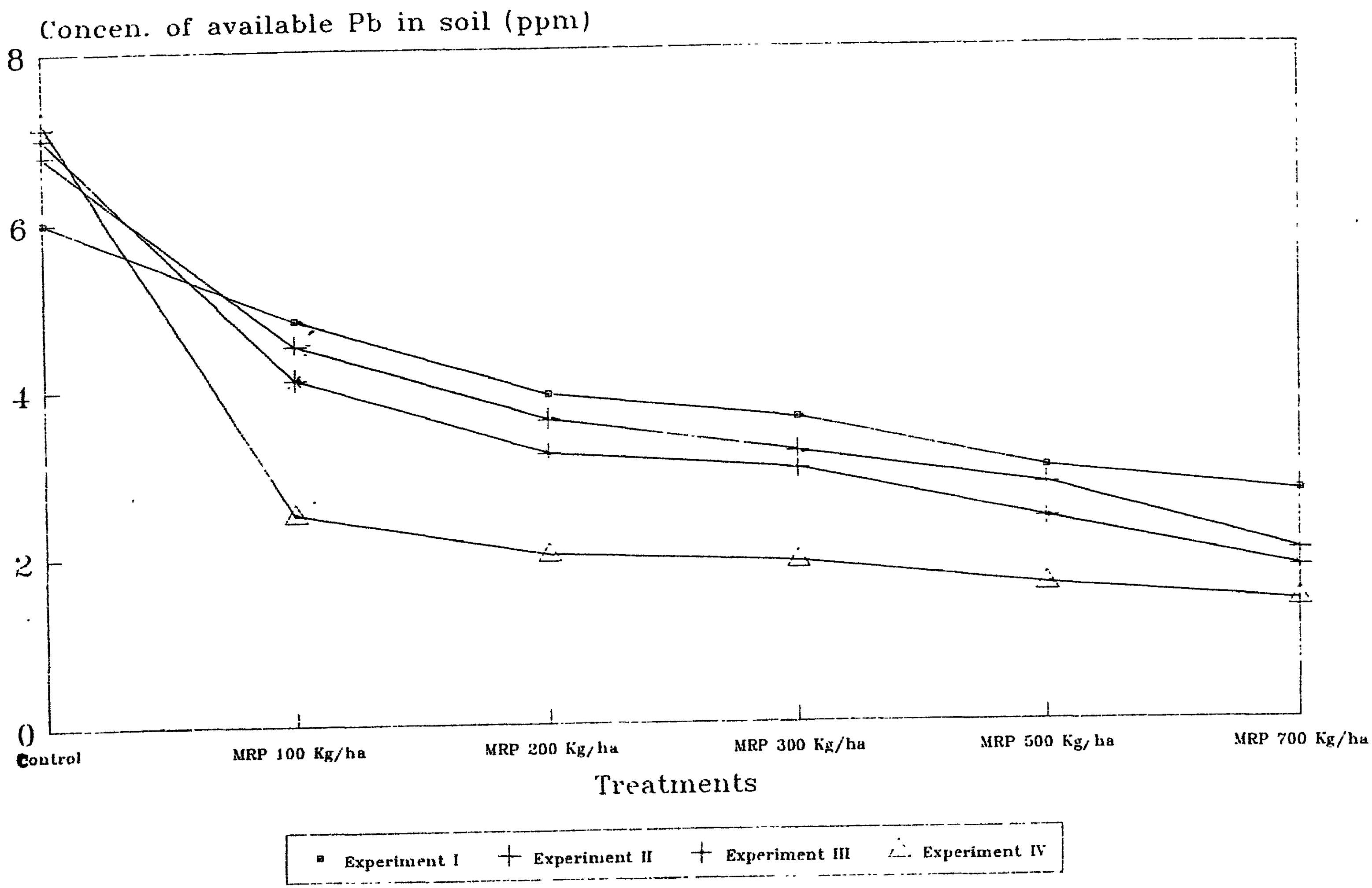

Fig. 6.4 Interaction of Pb and P in soil

Table 6.5 : Interation of Iron and Phosphorus

(in ppm)

Treatments	Experiment I	Experiment II	Experiment III	Experiment IV
	Available Fe	Available Fe	Available Fe	Available Fe
Control (Only Sewage irrigated soil	23.0	29.0	33.1	37.4
100 kg/ha MRP + Sewage irrigated soil	19.0	18.2	17.8	17.2
200 kg/ha MRP + Sewage irrigated soil	18.2	17.0	16.2	16.0
300 kg/ha MRP + Sewage irrigated soil	16.2	14.7	14.3	14.0
500 kg/ha MRP + Sewage irrigated soil	12.3	11.2	11.0	10.4
700 kg/ha MRP + Sewage irrigated soil	11.8	10.2	10.0	9.1
	r=0.67	r=0.71	r=0.83	r=0.87

Table 6.5 presents the interaction of phosphate and iron in controls, available Fe increased due to the supply of Fe through sewage. However, available Fe

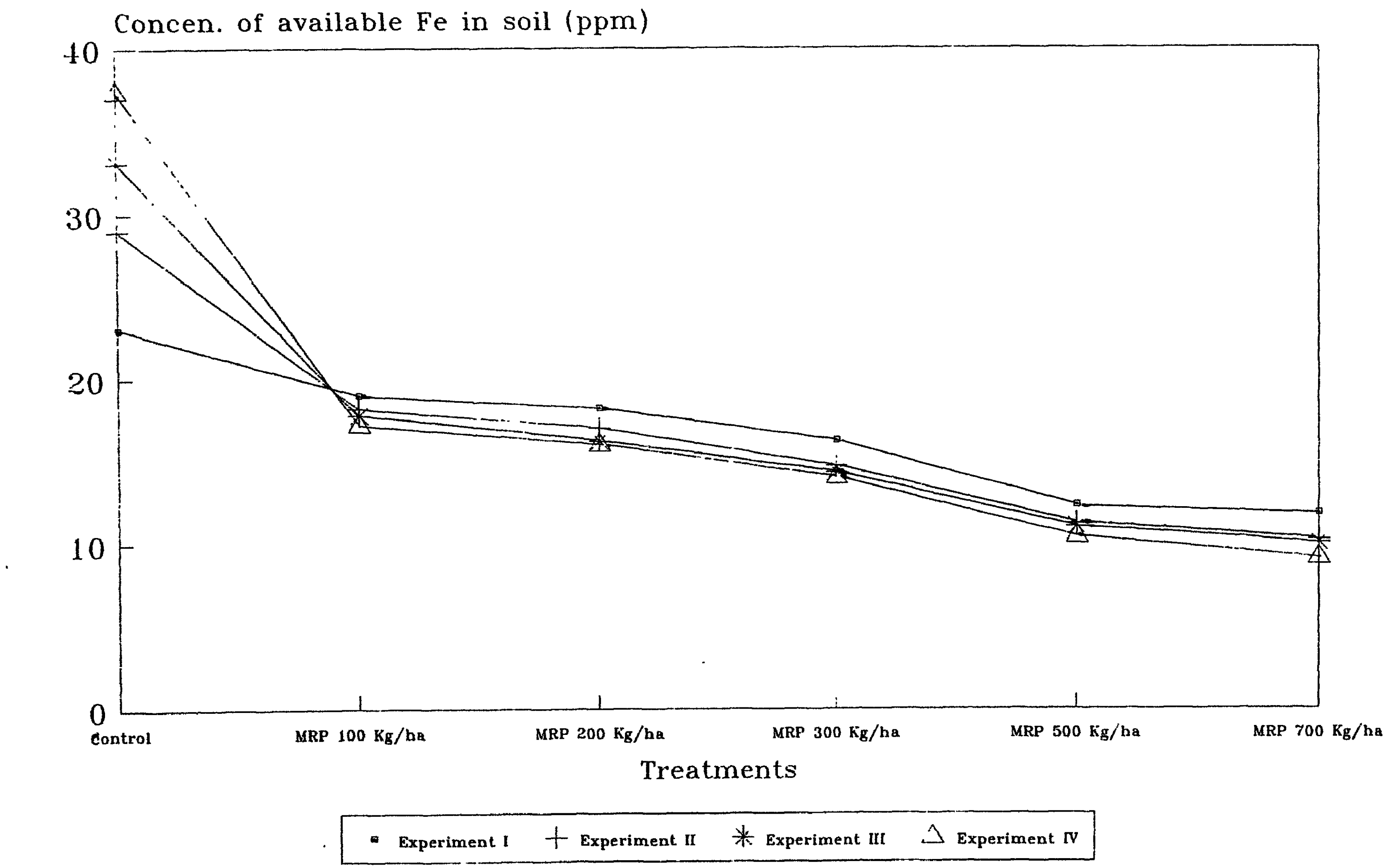

Fig. 6.5 Interaction between Fe and P in soil

showed a decrease with increasing doses of MRP, but the decrease in available Fe is not so marked as with Zn, Cr, Cu and Pb.

GENERAL DISCUSSION:

The availability results show that Zn, Cr, Cu, Pb and Fe in the soil is decreased as a result of adding increasing doses of MRP to the soil.

As Zn is a micronutrient, the crops must have utilized it for their growth leading to a decrease in available Zn in the soil. But at the same time, added MRP must have interacted with available Zn and thus helped in decreasing the available Zn. Such decrease in available Zn due to Zn x P interaction has been reported by others. (Takkar 1976, Safaya 1976, Bhogal et al. 1985, and Takkar et al. 1989). The available amounts of Cr, Cu, and Pb also must have decreased due to interaction with soluble P from MRP as a result of sewage irrigation. Similar results have been reported by Dev and Mann(1972), Gupta et al. (1983) and Takkar et al. (1986).

It is a fact that repeated irrigation with sewage must have added heavy metals to the soil. Decreased availability of heavy metals indicates that increasing

soluble phosphate from MRP must have interacted wit them. Thus phosphate from MRP is solubilized due t sewage and it combines with Zn, Cu and Fe and the reduces their availability in the soil. But even thi reduced availability is sufficient so that the uptak of heavy metals is even then high and even toxic though the toxicity has reduced to a very low level.

Hence the beneficial effect of adding MR alongwith sewage lies in the fact that it interact with the heavy metals present in the soil (from variou sources) and reduces their availability to crops. Thu it helps in moderating the toxic effect of heav metals, which would otherwise be taken up by the crop and then may prove injurious to animals and huma beings.

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CHAPTER VII

CHAPTER - VII

CHANGES IN SOIL:

Chemical characteristics of sewage water vary with the source of potable water supply, the sewage system, the season and the nature of industrial discharge into the system.

The trace elements or heavy metals are found in sewage water both in the suspended and in the liquid fractions. These associated with the suspended solids accumulate on the soil surface as the effluent infiltrates into the soil, while those dissolved in the liquid component penetrate into soil. The trace elements derived from both fractions interacts with soil components.

The existence of heavy metals in anionic form in soil could not be widely recognised until the last few years. According to Hodgson (1969) not only is all the mobile Fe normally chelated and so either uncharged or anionic, but so is all the mobile Cu, most of mobile Mn of neutral soils and up to one third of the mobile Zn. But this does not mean that fixation of the heavy metals as cations has been overemphasized.

The trace elements of heavy metals reaching soil plant system participate in different soil reactions the principal ones being ion exchange, precipitation, surface adsorption and organic complexing. Prediction of trace heavy element behaviour in soils can be made depending on the knowledge each of these reactions (Page et al. 1981).

Mc Bridge (1989) considered the following processes as determining the solubility of heavy metals in soil: (a) ion exchange on layer silicate (b) chemisorption on mineral surface (c) reduction, precipitation and solid solution (d) redox processes, taking into consideration oxidation of metals, metal oxides and dissolution of metals by organic materials (e) metal adsorption by organic matter and (f) speciation.

The most important single aspect of the reaction between heavy metals and soils is the effect of pH. Heavy metals are held far more firmly and less reversibly as the pH rises form 5.0 to 7.0.

Page et al (1981) reported that 'in general'

the solubility of cationic trace element species increases and that of anionic ones decreases with decreasing pH. Small changes in soil pH can result in major differences in the adsorption of trace elements on the soil surface (Jones and Jarvis 1981).

Williams et al. (1980) mentioned organic acids, amino acids fulvic acid, as well as biological systems and biological residues, as influencing trace element solubility in soils. The addition of organic matter was often found to decrease the sorption of trace elements on the soil.

Korte et al. (1976) found that the most useful information for predicting soil effectiveness for trace elements retention relates to soil texture, soil surface, area and the content of hydrous oxides and free lime. Soil clay has often been considered as a major factor determining trace element solubility.

Dowdy and Volk (1983) concluded that although some studies have noted movement of trace metals to layers below the soil surface or depth of incorporation it appears that only Zn has the potential to move in soils. Movement of heavy metals in soils will occur in

sandy, acid, low organic matter soils, subjected to heavy rainfall or irrigation. Open channels or cracks increase trace elements movement in soils, but elswhere such movement is usually limited.

Lead reacts with many soil constituents, such as clay, phosphate, carbonate, hydroxides, sesquioxides and organic matter, resulting in low availability of Pb. Jurinak and Santillan-Medrano (1974) attributed the high Pb retention to hydroxides and hydroxy phosphate in acid soils, and to carbonates in calcareous soils. Increasing the soil pH as well as the CEC and P levels resulted in a decrease in soil-Pb availability.

Addition of heavy metals to soils have usually been made in the presence of ample quantities of phosphate. Building up reserves of P is an early stage in improving agriculture, and applying the trace elements comes next in time. Zn deficiency in particular has occurred and continues to occur after adding ample P. Where sewage water containing heavy metal is applied to the land, some amounts of P are commonly present. The evidence of antagonism between individual heavy metals and P is present in soils, but the best evidence is that the antagonism is within the

plant rather than within soil. Some phosphates such as $Zn_3(PO_4)_2$ are too soluble to explain the disappearance of either Zn or P.

Analysis of soil after adding MRP to soil and growing crops is likely to afford clues regarding such interactions. Hence the present chapter is devoted to this problem.

EXPERIMENTAL:

Soil sample from control plot was taken before experiment and finally sample taken from various treated plots after four crops.

Samples were analysed for pH, organic carbon, available P_2O_5 and available heavy metals in order to findout the changes in the soil constituents.

Table 7.1 : Physico-chemical properties of Sheila Dhar Institute Experimental Farm Soil (Before experiments).

Properties		
1.	pH	7.3
2.	E.C. (d S^{m-1}) at 25°C	0.48
3.	CEC [Cmol (p^+) kg^{-1}]	21.5
4.	Organic carbon (%)	1.0
5.	Available N (%)	0.14
6.	Available Potash (kg/ha)	238
7.	Avilable Phosphorus (kg/ha)	9.0

Table 7.2 : Physico-chemical properties of sewage irrigated soil (after experiments during Sept. 1992 to April 1995).

Properties		
1.	pH	7.0
2.	E.C. (dS^{m-1}) at 25°C	0.51
3.	CEC [Cmol (p^{+}) kg^{-1}]	22.3
4.	Organic carbon (%)	1.632
5.	Available N (%)	0.19
6.	Available Potash (kg/ha)	243
7.	Available Phosphorus (kg/ha)	31.4

Table 7.3 : Comparative amounts of available heavy metals, before and after the experiments, in control plot soil (only sewage treated).

(ppm)

Heavy metals (DTPA extractable)	Before the experiments (Sept. 1992)	After the experiments (April 1995)
Zn	9.9	16.4
Cu	6.0	7.7
Cr	2.9	4.8
Pb	5.6	7.2
Fe	20.2	37.4

Table 7.4 :Amounts of available phosphorus in experimental plot soils.

Doses of added MRP (kg/ha)	Available P_2O_5 (kg/ha)			
	Experiment I	Experiment II	Experiment III	Experiment IV
Control (MRP 0)	9.90	10.00	9.10	9.90
MRP 100 kg/ha	13.50	14.80	17.80	19.10
MRP 200 kg/ha	15.00	16.50	24.00	27.80
MRP 300 kg/ha	18.10	20.95	29.85	36.15
MRP 500 kg/ha	26.80	28.10	35.21	43.20
MRP 700 kg/ha	29.95	31.10	39.00	52.00

RESULTS AND DISCUSSION:

The chemical analysis of soils before and after the experiments are given in tables 7.2 and 7.3.

The pH of the soil decreased after the experiments. This may be due to production of organic acids from organic matter and availability of

micronutrients/heavy metals.

The beneficiation of sewage use on EC, CEC, organic carbon, nitrogen, phosphorus and potash is also seen.

The results presented in table 7.2 show that organic carbon has increased by 0.623% as a result of sewage irrigation. There has been also an increase in N due to sewage irrigation, but the increases in available P_2O_5 are definitely due to MRP addition because negligible amount of P (0.02 kg/ha) is added through sewage water.

The available P_2O_5 data show that there is propertionate increase in available P_2O_5 with increase in added MRP. For example, where 700 kg MRP is added the total P_2O_5 added whould be 140 kg (20% P_2O_5 in MRP) but the increase in available P_2O_5 at the begining of the experiments comes to 20 kg/ha.

This value shows an increase of about 40 kg/ha at the end of four crops. Taking into consideration that three additions of MRP have been made, the value should have been 60 kg/ha. (Removal by crops is not

taken into account). This shows that MRP gradually becomes available and this increased available P_2O_5 can interact with the heavy metals being added to the soil through sewage irrigation.

Large uptake of heavy metals in the begining indicates the absence of soluble P in sewage as well as very little availability of MRP. However MRP grdually became available due to organic matter being added through sewage water and the microbial activity in the soil and this resulted in decreased availability of heavy metals.

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CHAPTER VIII

CHAPTER-VIII

SUMMARY

The four crops grown in order were fenugreek, spinach, fenugreek and radish. The plots were treated with different doses of Mussoorie rock phosphate (MRP). MRP was added in experiments I, III and IV and in experiment II residual effect was operative.

All the plots were irrigated by sewage water. At least 10 irrigations (about 10 liters per plot each time) were made.

In experiment I, the heights and yield of crop was maximum with highest dose of MRP (700 kg/ha) though lower doses of MRP also gave better response than control.

The uptake of toxic heavy metals (viz. Zn, Cr, Cu, Pb, and Fe) in control plots was higher than in MRP treated plots. This points to a possible interaction of heavy metals present in the sewage with added MRP (phosphate reacts with heavy metals).

The availability of P increased due to MRP additions, which helped the growth and yield of fenugreek.

In experiments II, the residual effect of MRP alongwith sewage irrigation is reflected in the form of greater heights and yield of spinach.

The concentration of heavy metals in control plots due to further additions of sewage should show increase. But the available heavy metals were depressed with increasing doses of MRP added to the plots, which led to decreased uptake of heavy metals by spinach in comparison to control.

In experiment III, the heights of fenugreek increased at all the stages of growth. The growth and yield of fenugreek were better than in experiment I. It is due to addition of nutrients by sewage irrigation and availability of phosphate.

The uptake of heavy metals showed similar trend as in experiments I and II. But in control it increased due to gradual additions of heavy metals through sewage irrigation.

The available Zn, Cu, Cr, Pb and Fe reduced with increasing doses of MRP, due to interaction as in experiments I and II.

In experiment IV, the heights and yield of radish were greater in MRP treatements than control. It may be due to effect of heavy metals accumulating in control plots and building up toxicity.

The content of heavy metals was very low in roots in comparison to leaves and was lower than in other experiments.

The interaction between heavy metals and P was very high due to high available amount of phosphate.

The soil on being analysed after the crops showed some interesting features. EC, CEC, N, P, K, increased but pH reduced. Especially organic carbon increased to 0.632%.

The available heavy metals viz. Zn, Cu, Cr, Pb and Fe increased by 6.3, 1.7, 1.8, 1.6 and 17.2 ppm respectively, in control.

Thus it can be recomended that the use of sewage along with MRP is better for growth and biomass of vegetable crops.

The MRP is a cheap phosphatic meterial which can

serve as an alternative for phosphate fertilizer. The residual effect of MRP is also visible.

It can also be sermised that the uptake of heavy metals reduced by such an interaction due to formation complexes with P and heavy metals.

Thus addtion of these heavy metals in food chain may be minimised and a better use of sewage water can be also made with a less harm.

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